The Reaction of Chloral with Methyl Ketones[1a]

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The condensation of chloral with four methyl ketones has been studied. Evidence is presented that 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I) is the sole product of the reaction of chloral with isobutyl methyl ketone thus establishing that condensation occurs at the methyl rather than at the methylene group adjacent to the carbonyl function of the ketone. The reaction of chloral with mesityl oxide in acetic acid as solvent leads to the formation of 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) and 2,2-dimethyl-6-(trichloromethyl)-tetrahydro-1,4-pyrone (III). In the presence of sodium acetate, II was the only product isolated. *p*-Toluenesulfonic acid catalyzes the cyclization of II to III. 1,1,1-Trichloro-2-hydroxy-4-pentanone (IV), prepared from chloral and acetone, reacts with benzaldehyde in the presence of *p*-toluenesulfonic acid to form 1,1,1-trichloro-6-phenyl-2,5-hexadien-4-one (V). The same compound is obtained by condensation of chloral with benzalacetone and subsequent acid-catalyzed dehydration of the resulting 1,1,1-trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (VI).

Aryltrichloromethylcarbinols have been shown to be versatile intermediates which can be converted into α-methoxy acids,[2] α-chloro acids,[3] and α-amino acids[4] by reaction with the appropriate nucleophile under basic conditions. The application of these reactions to the aliphatic series has been hindered by the lack of convenient methods of preparation of the alkyltrichloromethylcarbinols. The purpose of this research was to investigate the condensation of chloral with ketones and to study the reactions of the resulting 1,1,1-trichloro-2-hydroxy-4-alkanones as potential intermediates for the synthesis of the desired aliphatic trichloromethylcarbinols.

Some previous work on the condensation of chloral with aliphatic ketones has been reported and reviewed by Ledrut.[5,6] "Chloralacetone" and "chloralacetophenone" have been prepared from chloral and the corresponding ketone in glacial acetic acid or without solvent as early as 1892[7] and 1893.[8] In these two cases, no ambiguity exists with respect to the structure of the addition product since in both acetone and acetophenone there is only one reactive center in a position α to the carbonyl group. However, in the case of unsymmetrical alkyl methyl ketones, there is disagreement in the literature as to whether the chloral attacks the methyl or methylene group. Breusch and Keskin[9,10] prepared a series of 1,1,1-trichloro-2-hydroxy-4-alkanones from chloral and unsymmetrical alkyl methyl ketones. In order to establish at which carbon atom condensation had taken place, they treated 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I) with aqueous potassium hydroxide solution and reduced the reaction product with zinc and hydrochloric acid. A mixture melting point determination of the substance resulting from this reduction and β-isovalerylpropionic acid showed the two compounds to be identical, thus indicating that condensation had occurred at the methyl rather than the methylene group of the ketone. In spite of this evidence, a study of the condensation of chloral with ketones led Caujolle, Couturier, and Dulaurans[11] to the conclusion that ketones containing both a methyl and a methylene group adjacent to the carbonyl function react with chloral preferentially at the methylene group. Thus, they postulate that the reaction of chloral with ethyl methyl ketone leads to the formation of 1,1,1-trichloro-2-hydroxy-3-methyl-4-pentanone, $CH_3COCH(CH_3)CHOHCCl_3$.

To resolve this discrepancy in the literature and to investigate the reactivity of the 1,1,1-trichloro-2-hydroxy-4-alkanones, an extensive study of the reaction of chloral with isobutyl methyl ketone and three other methyl ketones was undertaken.

Results and Discussion

Chloral and Isobutyl Methyl Ketone.—The reaction of chloral with this typical unsymmetrical saturated ketone was studied in detail.

$$(CH_3)_2CHCH_2COCH_3 + CCl_3CHO \longrightarrow \underset{\text{I}}{(CH_3)_2CHCH_2COCH_2CHOHCCl_3}$$

Under optimum conditions, the reaction proceeds to approximately 60% completion over a period of 4 days at 100°. Heating for much longer periods is undesirable because of the formation of dark-colored side products. Keeping reaction time and temperature constant (19 hr and 103°, respectively), the condensation of the two carbonyl compounds in glacial acetic acid as solvent gives a 15% yield of 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I) in the absence of any base catalyst, a 31% yield in the presence of sodium acetate, and a 42% yield when the reaction is carried out in propionic acid in the presence of sodium propionate. This indicates clearly that the reaction is base catalyzed, the more pronounced rate-enhancing effect of sodium propionate being due to its higher basicity. Potassium acetate is no more effective as a catalyst than sodium acetate while triethylamine is only half as effective. Stronger bases cannot be used because they destroy the chloral. In addition to catalyzing the desired condensation, sodium acetate and sodium propionate inhibit the formation of the dark-colored by-products. Only trace amounts of the product I were obtained when formic acid, acetic anhydride, or toluene (with *p*-

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(1) (a) The work herein described formed part of the Ph.D. Thesis of E. Kiehlmann, University of Maryland, 1964. (b) Gillette-Harris Research Fellow, 1962–1963; Celanese Research Fellow, 1963–1964.

(2) W. Reeve and C. W. Woods, *J. Am. Chem. Soc.*, **82**, 4062 (1960).

(3) J. Jocicz, *J. Russ. Phys. Chem. Soc.*, **29**, 97 (1897); *Chem. Zentr.*, **68**, 1013 (1897).

(4) W. Reeve and L. W. Fine, *J. Org. Chem.*, **29**, 1148 (1964).

(5) J. Ledrut and G. Combes, *Ind. Chim. Belge*, **19**, 120 (1954).

(6) J. Ledrut and G. Combes, *ibid.*, **27**, 635 (1962).

(7) W. Koenigs, *Chem. Ber.*, **25**, 729 (1892).

(8) J. Wislicenus and T. Kircheisen, *ibid.*, **26**, 908 (1893).

(9) F. L. Breusch and H. Keskin, *Arch. Biochem. Biophys.*, **18**, 305 (1948).

(10) H. Keskin, *Rev. Fac. Sci. Univ. Istanbul.*, **15a**, No. 1, 54 (1950); *Chem. Abstr.*, **45**, 2904 (1951).

(11) F. Caujolle, P. Couturier, and C. Dulaurans, *Bull. Soc. Chim. France*, **17**, 19 (1950).

toluenesulfonic acid as catalyst) were used as solvents. Water inhibits the reaction by forming chloral hydrate. Excess chloral may be used as solvent, but the dark side products are at a minimum when the ketone is in slight excess.

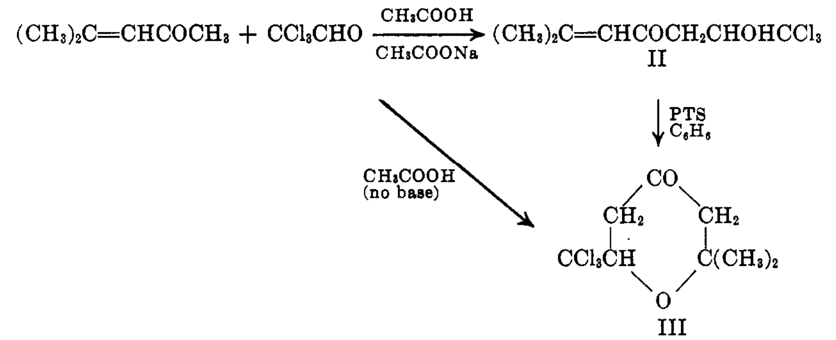
The optimum conditions involve the condensation of 1 mole of chloral with 1.25 moles of isobutyl methyl ketone in the presence of 2 moles of propionic acid and 0.25 moles of sodium propionate at 100° for 4–5 days; 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I) was obtained in 59% yield. Substituting acetic acid and sodium acetate, a 54% yield was isolated after 4 days at 100°. When the unreacted, volatile, starting materials were isolated by distillation and recycled as part of a second reaction, there was obtained sufficient additional product to raise the over-all yield to 80% of the theoretical.

All of the evidence at hand suggests that the reaction involves the slow, base-catalyzed formation of an anion from the ketone, and the addition of this anion to the carbonyl group of the chloral.[12] The equilibrium point, determined by subjecting the final product to the same reaction conditions as employed in its preparation, lies at the extreme right. This indicates kinetic rather than thermodynamic control of the condensation reaction. No simple kinetic picture was observed; the reaction slows down abnormally after several days of heating, presumably because of the inhibiting effect of the by-products.

In addition to the evidence advanced by Breusch and Keskin[9] for the structure of the ketone chloral condensation product, the following results verified the validity of their structural assignments. Mesityl oxide reacts with chloral to yield 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) the structure of which was uniquely determined from its nmr spectrum and its conversion to a cyclic tetrahydropyranone (III). Hydrogenation of the carbon–carbon double bond in compound II gave 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I) identical with the compound prepared from isobutyl methyl ketone and chloral. Also, isobutyl methyl ketone reacts with *n*-butyl glyoxylate to form a hydroxy ester which was converted to the known β-isovalerylacrylic acid (VII) identical with the β-isovalerylacrylic acid obtained from the 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I) by treatment with methanolic potassium hydroxide at 50°. Finally, the nmr spectra of all the compounds obtained were consistent with the assigned structures.

Chloral and Mesityl Oxide.—For the reaction of mesityl oxide with chloral, no ambiguity is to be expected with respect to the structure of the addition product since in mesityl oxide there is only one reactive center where condensation can take place α to the carbonyl group. However, it was found experimentally that in the presence of sodium acetate or sodium propionate, 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) is formed exclusively while in the absence of a base catalyst, the reaction results in either the formation of 2,2-dimethyl-6-(trichloromethyl)tetrahydro-1,4-pyrone (III) alone (at 98°) or, when carried out at a lower temperature (70°), a mixture of II and III (Scheme I). A 41% yield of II was obtained when a mixture of chloral, mesityl oxide (slight excess) and 25 mole % sodium propionate was heated to 73° for 4 days in propionic acid as solvent. This represents a considerable improvement over the 10% yield reported in the literature.[9]

SCHEME I



$$(CH_3)_2C{=}CHCOCH_3 + CCl_3CHO \xrightarrow[CH_3COONa]{CH_3COOH} (CH_3)_2C{=}CHCOCH_2CHOHCCl_3$$

The structures of II and III were established by qualitative tests and spectrographic analysis. While 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) reacts rapidly with bromine in carbon tetrachloride and with aqueous permanganate solution indicating the presence of a double bond, 2,2-dimethyl-6-(trichloromethyl)tetrahydro-1,4-pyrone (III) is inert to these reagents. The characteristic absorption bands for OH and C=C at 3400 and 1625 cm^{-1}, respectively, are observed in the infrared spectrum of II but absent in the spectrum of III. The nuclear magnetic resonance spectrum of III, discussed in detail in the Experimental Section, shows clearly the presence of a rigid ring system with restricted rotation, and is in agreement with the structure of a substituted tetrahydro-1,4-pyrone. As described in the preceding paragraph, hydrogenation of II over palladium-on-carbon catalyst yields quantitatively 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I). When 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) is refluxed in benzene in the presence of 10 mole % *p*-toluenesulfonic acid (PTS), cyclization takes place to form 2,2-dimethyl-6-(trichloromethyl)-tetrahydro-1,4-pyrone (III) in 57% yield. This cyclization and the formation of both II and III when mesityl oxide, chloral, and acetic acid are heated to 70° for 4 days indicate that II is a true intermediate in the formation of III. The cyclization of 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) can be visualized as an internal Michael reaction with the proton of the hydroxyl group attacking the double bond activated by

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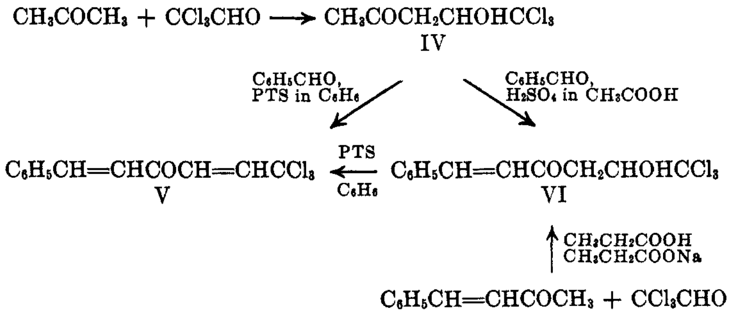
[12] For a detailed discussion of this mechanism and the alternative possibility of a fast equilibrium between the ketone and its carbanion preceding the rate-determining reaction of the carbanion with chloral, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp 389–391.

the adjacent carbonyl function. The acid catalyst helps to polarize the double bond by coordination with the oxygen of the carbonyl group.

Chloral and Acetone.—The reaction of acetone with chloral has been studied previously by Koenigs[7] and by Caujolle.[11] Our work has shown that this reaction carried out under the same conditions as used with isobutyl methyl ketone gives, after 4 days of reflux, a 50% yield with a sodium acetate–acetic acid catalyst–solvent system, and a 45% yield when sodium propionate and propionic acid are used. Although acetone has two active methyl groups, the reaction stops completely after the addition of one molecule of chloral. The product, therefore, still contains one reactive methyl group α to the carbonyl function and this methyl group, under different experimental conditions, undergoes further condensation reactions. Benzaldehyde reacts with 1,1,1-trichloro-2-hydroxy-4-pentanone (IV) (Scheme II) in acetic acid in the presence of sulfuric acid to form 1,1,1-trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (VI) in 3% yield while with benzene as solvent and p-toluenesulfonic acid as catalyst, 1,1,1-trichloro-6-phenyl-2,5-hexadien-4-one (V) was isolated in 17% yield. No trace of either condensation product V or VI could be isolated when acetic acid and sodium acetate were employed as catalyst–solvent system. 1,1,1-Trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (VI) was also obtained by condensation of chloral with benzalacetone.[11,13] Compound VI does not form a tetrahydropyrone derivative on treatment with p-toluenesulfonic acid in refluxing benzene, but dehydrates to 1,1,1-trichloro-6-phenyl-2,5-hexadien-4-one (V) in 70% yield. The structure of V follows from the analytical data, the nmr spectrum which shows only olefinic protons, and the infrared spectrum which shows typical bands corresponding to the carbon–carbon double bonds and the carbonyl group, but no hydroxyl absorption. The fact that 1,1,1-trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (VI), in contrast to II, does not form a tetrahydropyrone derivative is probably due to mesomeric stabilization of the unsaturated system in V.

Scheme II



The noncyclic ketotrichloromethylcarbinols I, II, and IV have two unexpected properties. They do not react with 2,4-dinitrophenylhydrazine, presumably because of the bulky trichloromethylcarbinol group. Second, they do not form isolable α,β-unsaturated ketones on refluxing a benzene solution with 3 mole % p-toluenesulfonic acid; thus, after 48 hr, 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I) could be recovered in 62% yield.

Experimental Section

All melting points are corrected. Analyses were performed by Dr. Franz Kasler. The infrared spectra were recorded on a Beckman IR-5 spectrometer using a Nujol mull of the solid as a thin film between sodium chloride plates. The nuclear magnetic resonance were run by Mrs. Helen Sing on a Varian DP-60 spectrometer at a radio frequency of 56.4 Mc/sec. The external magnetic field was varied in the immediate vicinity of 13246 gauss. Tetramethylsilane was used as internal standard and carbon tetrachloride as the solvent.

1,1,1-Trichloro-2-hydroxy-6-methyl-4-heptanone (I).—A mixture of 148 g (2.0 moles) of propionic acid, 24 g (0.25 mole) of sodium propionate, 125 g (1.25 moles) of isobutyl methyl ketone, and 148 g (1.0 mole) of anhydrous chloral[14] was heated in a flask immersed in a steam bath for 108 hr. Solvent and unreacted starting materials were removed by distillation under reduced pressure. The dark distillation residue was dissolved in 350 ml of ether, washed with water and sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent by vacuum distillation and recrystallization from cyclohexane gave 146 g (59% of theory) of 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone: mp 86–87° (lit.[9] mp 86–87°); $\nu_{\max}^{\mathrm{Nujol}}$ 3400, 2855, 1705, 1470, 1405, 1375, 1325, 1125, 1000, 913, 805, 787, and 700 cm^{-1}; nmr, $\nu_{\max}^{\mathrm{CCl_4}}$, τ 9.02, doublet [6 protons, $(\mathrm{C}H_3)_2\mathrm{CH}$]; 5.52, multiplet (2 protons, $\mathrm{C}HOH\mathrm{CCl_3}$); 6.94, multiplet (2 protons, $\mathrm{COC}H_2\mathrm{CHOH}$); 7.63, multiplet [3 protons, $(\mathrm{CH_3})_2\mathrm{C}H\mathrm{C}H_2\mathrm{CO}$].

1,1,1-Trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II).—A mixture of 148 g (2.0 mole) of propionic acid, 24 g (0.25 mole) of sodium propionate, 123 g (1.25 moles) of commercial mesityl oxide, and 148 g (1.0 mole) of anhydrous chloral was heated at 73° for 91 hr. Maintaining the bath temperature below 83°, solvent, and unreacted starting materials were distilled under reduced pressure, and the brown residue was taken up in 400 ml of ether. Extraction with water, removal of the ether *in vacuo*, and distillation using a short, air-cooled condenser gave 150 g of crude product, bp 137–152° (0.7 mm), from which 100 g (41% of theory) of pure 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II), mp 87–89° (lit.[9] mp 89–90°), was obtained by recrystallization from cyclohexane: $\nu_{\max}^{\mathrm{Nujol}}$ 3400, 2900, 1685, 1625, 1485, 1390, 1315, 1285, 1210, 1110, 1065, 1005, 935, 905, 813, 795, and 735 cm^{-1}; nmr, $\nu_{\max}^{\mathrm{CCl_4}}$, τ 8.21, singlet, and 7.96, singlet [6, $(\mathrm{CH_3})_2\mathrm{C{=}C}$]; 7.04, multiplet (2, $\mathrm{COCH_2}$); 5.27, multiplet (2, CHOH); 3.94, singlet (C=CH).

Anal. Calcd for $C_8H_{11}Cl_3O_2$: C, 39.13; H, 4.52; Cl, 43.32. Found: C, 39.02; H, 4.80; Cl, 43.51.

Hydrogenation of 1,1,1-Trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II).—A solution of 5.0 g (0.02 mole) of 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one in ethanol was hydrogenated over palladium-on-carbon catalyst at room temperature and 40 psi of hydrogen pressure. Filtration of the reaction mixture, evaporation of the solvent, and recrystallization of the residue from cyclohexane gave 1,1,1-trichloro-2-hydroxy-6-methyl-4-heptanone (I), mp 86–88°, in quantitative yield.

2,2-Dimethyl-6-(trichloromethyl)tetrahydro-1,4-pyrone (III).—A mixture of 60 g (1.0 mole) of glacial acetic acid, 49 g (0.5 mole) of mesityl oxide, and 74 g (0.5 mole) of anhydrous chloral was heated at 98° (steam bath) for 20 hr. The black residue left after removal of the solvent and excess reagents by vacuum distil-

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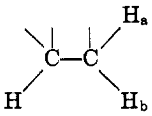
(13) A. Roedig and E. Klappert, *Ann. Chem.*, **608**, 126 (1957).

(14) Anhydrous chloral was prepared from the commercially available material (Matheson Coleman and Bell) by distillation from phosphorus pentoxide.

lation was treated with boiling ether and filtered. Cooling of the concentrated filtrate to −16°, filtration, and recrystallization from ether and cyclohexane gave 13.2 g (11% of theory) of pure 2,2-dimethyl-6-(trichloromethyl)tetrahydro-1,4-pyrone (III): mp 79–81°; $\nu_{\max}^{\text{Nujol}}$ 2900, 1725, 1465, 1380, 1315, 1280, 1255, 1205, 1125, 1095, 970, 895, 870, 855, 820, 770, and 670 cm^{-1}; nmr, $\nu_{\max}^{\text{CCl}_4}$, τ 8.88, singlet, and 8.68, singlet [6, $(CH_3)_2C$]; 7.70 and 7.28, multiplets (4, CH_2COCH_2); 5.75, quartet [$OCH(CCl_3)$-CH_2]. This quartet constitutes the typical ABX pattern of a proton split by two nonequivalent protons incorporated in a rigid ring system.



Anal. Calcd for $C_8H_{11}Cl_3O_2$: C, 39.13; H, 4.52; Cl, 43.32. Found: C, 39.25, H, 4.61; Cl, 43.15.

Reaction of Mesityl Oxide with Chloral in Acetic Acid at 70°.—A mixture of 120 g (2.0 moles) of glacial acetic acid, 123 g (1.25 moles) of mesityl oxide, and 148 g (1.0 mole) of anhydrous chloral was heated at 70° for 96 hr. Solvent and unreacted starting materials were removed by distillation under reduced pressure. Distillation of the dark residue gave 132 g of crude product, bp 111–142° (1 mm), from which 110 g (45% of theory, based on $C_8H_{11}Cl_3O_2$) of white material, mp 58–75°, was obtained by recrystallization from cyclohexane. Nuclear magnetic resonance and infrared spectral analysis revealed that this material consisted of approximately 45% 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) and 55% 2,2-dimethyl-6-(trichloromethyl)-tetrahydro-1,4-pyrone (III). Separation of the two components is possible by fractional crystallization from ethanol.

2,2-Dimethyl-6-(trichloromethyl)tetrahydro-1,4-pyrone (III) from 1,1,1-Trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II).—A solution of 24.5 g (0.10 mole) of 1,1,1-trichloro-2-hydroxy-6-methyl-5-hepten-4-one (II) and 2.0 g (0.01 mole) of *p*-toluenesulfonic acid monohydrate in 160 ml of benzene was vigorously refluxed for 10 hr. After cooling, the reaction mixture was washed with water and sodium bicarbonate solution, and dried; the solvent was removed by vacuum distillation. Recrystallization of the black residue from cyclohexane gave 14.0 g (57% of theory) of 2,2-dimethyl-6-(trichloromethyl)tetrahydro-1,4-pyrone (III): mp 79–80°.

1,1,1-Trichloro-2-hydroxy-4-pentanone (IV).—A mixture of 120 g (2.0 moles) of glacial acetic acid, 72.5 g (1.25 moles) of acetone, 20.0 g (0.25 mole) of anhydrous sodium acetate, and 148 g (1.0 mole) of anhydrous chloral was heated at 88° for 94 hr. Removal of solvent and unreacted starting materials by distillation at 12 mm followed by high-vacuum distillation gave 107 g of crude product, bp 100–115° (1 mm), from which 102.7 g (50% of theory) of 1,1,1-trichloro-2-hydroxy-4-pentanone (IV), mp 73–74.5° (lit.[7,11] mp 75–76°), was obtained by recrystallization from cyclohexane: $\nu_{\max}^{\text{Nujol}}$ 3300, 2860, 1705, 1450, 1370. 1310, 1275, 1215, 1170, 1110, 1020, 988, 870, 825, 805, and 760 cm^{-1}.

1,1,1-Trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (VI).—A mixture of 60 g (1.0 mole) of glacial acetic acid, 12.0 g (0.15 mole) of anhydrous sodium acetate, 91.3 g (0.625 mole) of benzalacetone, and 74 g (0.5 mole) of chloral was heated at 80° for 24 hr. Solvent and unreacted starting materials were removed by vacuum distillation. The brown, solid distillation residue was dissolved in 420 ml of ether, washed with water and sodium bicarbonate solution, and dried. Evaporation of the ether and recrystallization from cyclohexane and ethanol, successively, gave 67.4 g (22% of theory) of 1,1,1-trichloro-2-hydroxy-6-phenyl-5-hexen-4-one: mp 101.5–102.5° (lit.[11] mp 100°).

1,1,1-Trichloro-6-phenyl-2,5-hexadien-4-one (V) from 1,1,1-Trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (VI).—A solution of 29.4 g (0.1 mole) of 1,1,1-trichloro-2-hydroxy-6-phenyl-5-hexen-4-one (VI) and 2.0 (0.01 mole) of *p*-toluenesulfonic acid monohydrate in 160 ml of benzene was vigorously refluxed for 10 hr. The black reaction mixture was washed with saturated sodium chloride solution, dried, and the solvent was removed by vacuum distillation. Recrystallization of the crude product from cyclohexane and ether, and work-up of the mother liquors gave 19.3 g (70% of theory) of yellow 1,1,1-trichloro-6-phenyl-2,5-hexadien-4-one (V): mp 94–95° (lit.[13] mp 95°).

1,1,1-Trichloro-6-phenyl-2,5-hexadien-4-one (V) from 1,1,1-Trichloro-2-hydroxy-4-pentaneone (IV) and Benzaldehyde.—A solution of 10.6 g (0.1 mole) of freshly distilled benzaldehyde, 20.6 g (0.1 mole) of 1,1,1-trichloro-2-hydroxy-4-pentanone (IV), and 1.0 g (0.005 mole) of *p*-toluenesulfonic acid monohydrate in 160 ml of benzene was vigorously refluxed in a 250-ml flask equipped with Dean–Stark trap, reflux condenser, and calcium chloride tube. Heating was stopped when 1.8 ml (0.1 mole) of water had accumulated in the trap. The mixture was washed with water and sodium bicarbonate solution, and dried; the solvent was evaporated to give 26 g of black, crude product from which 4.7 g (17% of theory) of 1,1,1-trichloro-6-phenyl-2,5-hexadien-4-one (V), mp 95–96°, was obtained after several recrystallizations from cyclohexane and ether.

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Pyrone Series. VII.[1] Intermediates in the Synthesis of Polysubstituted 2-Pyrones

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The thermolabile Michael addition products formed together with 4,5,6-triaryl-2-pyrones have been shown to be ψ esters V. Their β,γ-unsaturated δ-lactonic structure accounts for their acid-catalyzed alcoholysis to the δ-keto esters VIII, and pyrolysis to the 1-alkoxytriarylbutadienes IX which give unsaturated ketones X on acid hydrolysis.

In the course of our syntheses of 4,5,6-triaryl-2-pyrones,[2a] 4,6-diaryl-5-methoxy-2-pyrones,[2b] and 4,6-diaryl-5-phenoxy-2-pyrones,[2c] evidence was sought for intermediate Michael addition products. We found, however, that only the pyrones VIa–c were accompanied by intermediate adducts of ethyl phenylpropiolate I (R = Et) (Scheme I) and the deoxybenzoins IIa–c.

Previously, we formulated these adducts as *trans-β*-desylcinnamic esters IIIa–c (R = Et), whereas the 5-oxo-3,4,5-triarylpent-2-enoic esters (VIIa,b, R = Me), obtained *via* fission of the corresponding pyrones VIa,b,[2a] were reckoned as the analogs of the hypothetical intermediate *cis* adducts IIIa,b (R = Et). The 5-oxo-3,4,5-triarylpent-3-enoates (VIIIa,b, R = Me)[2a] obtained during the course of the pyrone fission were

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[1] Part VI: I. El-Sayed El-Kholy, M. M. Mishrikey, F. K. Rafla, and G. Soliman, *J. Chem. Soc.*, 5153 (1962).

[2] (a) G. Soliman, *et al.*, *J. Chem. Soc.*, 2911 (1955); (b) *ibid.*, 2588 (1959); (c) *ibid.*, 4490 (1961).