From the aqueous layer was eventually isolated chaksine iodide in 1.1% yield. The ethereal layer was dried and evaporated to afford 20 g. (2%) of a dark viscous neutral oil.

Saponification of 75 g. of neutral oil *via* ethanolic sodium hydroxide followed by the usual workup afforded 3.9 g. of a neutral, orange semisolid mass. The latter was crystallized from ethanol as a colorless solid (1.1 g.), m.p. 134–136°. Recrystallization from ethanol afforded β-sitosterol as colorless plates, m.p. 137–138°, $\alpha]_D^{25}$ −30° (*c*, 1.1 $CHCl_3$). (Lit.,[4] m.p. 136–137°, $\alpha]_D^{25}$ −36.) Its infrared spectrum was superimposable on that of an authentic sample.

Anal. Calcd. for $C_{29}H_{50}O$: C, 84.0; H, 12.1. Found: C, 84.1; H, 11.9.

The mother liquors remaining after the crystallization of β-sitosterol were evaporated to dryness, then acetylated with acetyl chloride and pyridine. The crude mixture (2.0 g.) was chromatographed on neutral alumina (40 g.) to yield 0.7 g. of β-sitosteryl acetate, m.p. 127–128°, and 0.3 g. of a colorless viscous liquid, n_D^{27} 1.4954. It showed absorption in the infrared characteristic of a saturated hydrocarbon, $\lambda_{max.}$ 2950 cm^{-1}, 2880, 1460, 1380.

β-Sitosterol acetate was prepared by treating 150 mg. of β-sitosterol with 8 ml. of acetyl chloride and a few drops of pyridine at 0°. Pouring the mixture on ice gave a colorless precipitate which crystallized from ethanol as colorless needles, m.p. 126–128°. (Lit.,[4] m.p. 125–126).

Anal. Calcd. for $C_{31}H_{52}O$: C, 81.5; H, 11.5. Found: C, 81.1; H, 11.4.

To 100 mg. of β-siterosterol in 3 ml. of pyridine at 0° was added 3 ml. of benzoyl chloride. The solution was warmed on a steam bath for 10 min. after the initial exothermic reaction had subsided. The solution was poured on ice and the colorless precipitate removed by filtration. The *β-sitosterol benzoate* crystallized from ethanol as colorless needles, m.p. 139–140°. (Lit.,[4] m.p. 145°).

Dihydro-β-sitosterol (*Stigmastanol*). To 100 mg. of platinum oxide in 13 ml. of acetic acid and 27 ml. of ethyl acetate was added 200 mg. of β-sitosterol and the mixture was shaken for 10 hr. under 40 lbs. of hydrogen pressure. The catalyst was filtered and the filtrate added to water to afford a colorless precipitate which crystallized from ethanol as colorless plates, m.p. 139–140°, depressed to 121–130° on admixture with β-sitosterol, $\alpha]_D^{25}$ +30° (*c*, 0.9 $CHCl_3$). (Lit.,[4] m.p. 138–139°, $\alpha]_D^{20}$ + 25°).

Anal. Calcd. for $C_{29}H_{52}O$: C, 83.6; H, 12.6. Found: C, 83.5; H, 12.4.

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Chemistry of Lactones. II. Reaction of 2-Phenyl-4-benzylidene-5(4*H*)oxazolone with Benzene under Friedel-Crafts Conditions

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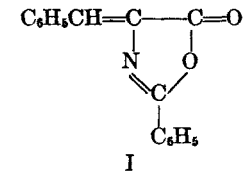
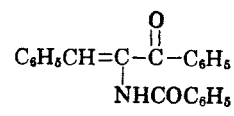
Oxazolones are often considered similar to cyclic anhydrides in their chemical reactions and might be expected to behave as acylating agents when treated with aromatic hydrocarbons in the presence of anhydrous aluminum chloride. Thus, succinic anhydride reacts with benzene under these conditions to form 3-benzoylpropionic acid. It was therefore of interest to study this reaction using 2-phenyl-4-benzylidene-5(4*H*)oxazolone (I) in place of anhydride. I has the added feature of an α,β-unsaturated carbonyl system.

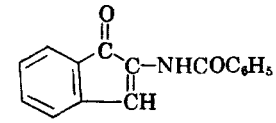


I

By analogy with cyclic anhydrides, it might be anticipated that I would react with benzene to give either 2-benzamidobenzalacetophenone (II) or 2-benzamidoindenone (III), formed by intramolecular cyclization.[2]

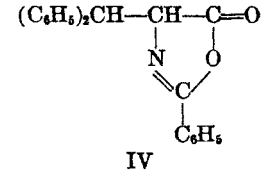


II



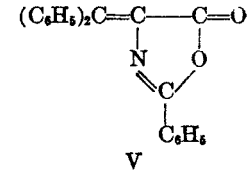
III

However, we did not isolate either II or III, the sole product being the saturated azlactone, 2-phenyl-4-diphenylmethyl-5(4*H*)oxazolone (IV), arising by 1,4 addition of benzene. The yield of IV after recrystallization was 62%.



IV

This saturated azlactone has not been described previously and compounds with this type of structure are not readily obtainable by other routes, especially since attempts to prepare the unsaturated precursor, V, have failed.



V

The isolation of IV suggests the possibility of preparing interesting new compounds containing the diphenylmethyl moiety.

The structure of IV was established by elemental analysis, infrared and ultraviolet spectra, and by formation of the benzylamide by aminolysis.

Whereas I exhibits a strong lactone carbonyl band at 1785 $cm.^{-1}$,[3a] typical of β,γ-unsaturated

(1) From the M.S. thesis of L.M.H., to be submitted to the Graduate School of Illinois Institute of Technology, 1958.

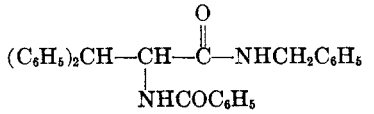
(2) M. S. Newman and L. M. Joshel, *J. Am. Chem. Soc.*, 62, 972 (1940).

(3) (a) H. W. Thompson, R. R. Brattain, H. M. Randall, and R. S. Rasmussen in *The Chemistry of Penicillin*, Princeton University Press, Princeton, N. J., 1949, p. 387. (b) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

γ-lactones,[3b] and >C=N absorption[3a] at 1650 cm.$^{-1}$, IV shows strong absorption at 1810 cm.$^{-1}$ and 1645 cm.$^{-1}$ The latter bands are almost identical with those observed for the 4-isopropyl analog[3a] and this shift of carbonyl absorption is consistent with removal of the conjugation created by attachment of an exocyclic double bond in the 4-position, as in I. It has also been shown that the frequency of the >C=N stretching mode is not appreciably affected by changes in the 4-position of these oxazolones.[3a]

The ultraviolet spectrum further supports structure IV. The intense maximum observed with I at 360 mμ has been attributed to the $C_6H_5CH{=}C(-N{=}C(-C_6H_5)-)$ chromophore.[4] The disappearance of this maximum in IV is evidence that this chromophore is absent, whereas the presence of λ_{max}^{EtOH} 245 mμ (ε 5450) is characteristic of the *N*-benzylidene group, $-N{=}C(-C_6H_5)-$.[5] The end absorption observed is also typical of such oxazolones.[5]

Saturated azlactones are generally very susceptible to hydrolysis and particularly to aminolysis.[6] However, IV was stable to a boiling water-acetone mixture, but reacted readily with benzylamine to form the 2-benzamidobenzylamide, VI, in nearly quantitative yield. The formation of an amide has at times been the sole evidence of the presence of an oxazolone and benzylamine is used for determining the proportion of oxazolone in a mixture ("azlactone equivalent").[7]



VI

In contrast to these results, I reacts with phenylmagnesium bromide by ring opening followed by 1,2-addition to give the tertiary alcohol.[8] Results of similar studies on the structurally related α-benzylidene-γ-phenyl-Δ β,γ-butenolide will be reported in a forthcoming paper and compared with those observed with the oxazolone.

EXPERIMENTAL[9]

Reaction of 2-phenyl-4-benzylidene-5(4H)-oxazolone (I) *with benzene.* In a 1-l., round-bottom flask, fitted with a mechanical stirrer, dropping funnel, and reflux condenser, were placed 9.5 g. (0.072 mole) of anhydrous aluminum chloride in 125 ml. of dry, thiophene-free benzene. The mixture was cooled to 10° and stirred for 1 hr. To this solution was added dropwise with stirring a solution containing 6 g. (0.024 mole) of 2-phenyl-4-benzylidene-5(4*H*)oxazolone in 125 ml. dry benzene, the temperature being maintained at 10–20° during the addition. The mixture turned brick red. When all of the oxazolone had been added, the mixture was stirred for an additional 3 hr. at room temperature. The complex was decomposed with 250 ml. dilute (1:15) HCl and two clear layers were obtained. The benzene layer was separated, the aqueous layer extracted with benzene, and the combined benzene extracts washed with dilute HCl, then with water until neutral to litmus. Benzene was removed by evaporation on a steam bath to give a yellow oil which was dissolved in ether and on addition of petroleum ether formed a light yellow precipitate. The product was recrystallized from 95% ethanol to give 4.8 g. (62%) of light yellow crystals, m.p. 158–159°.

Anal. Calcd. for $C_{29}H_{17}NO_2$: C, 80.71; H, 5.24; N, 4.28. Found: C, 80.87; H, 5.23; N, 4.25.

Reaction of 2-phenyl-4-diphenylmethyl-5(4H)-oxazolone (IV) *with benzylamine.* A mixture of 1.96 g. (0.006 mole) of oxazolone in 10 ml. dry benzene and 0.64 g. (0.06 mole) of benzylamine was heated under reflux for 30 min. On cooling, white crystals separated, which were washed with petroleum ether and recrystallized from 85% ethanol (H_2O as diluent) to give 2.4 g. (92%) of VI, m.p. 260–261°.

Anal. Calcd. for $C_{29}H_{26}N_2O_2$: N, 6.45. Found: N, 6.57.

Spectral measurements and analyses. Infrared spectra were obtained on a Perkin-Elmer 21 spectrophotometer and Perkin-Elmer "Infracord." The samples were examined either as Nujol mulls or by use of a KBr disk.

Ultraviolet spectra were measured in 95% ethanol using a Beckman DK-2 spectrophotometer.

The elemental analyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

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(5) R. B. Woodward, A. Neuberger, and N. R. Trenner, in *The Chemistry of Penicillin*, Princeton University Press, Princeton, N. J., 1949, p. 429.

(6) (a) H. E. Carter in *Org. Reactions*, III, 215 (1946). (b) E. Baltazzi, *Quart. Revs.* IX, No. 2 (1955), p. 160.

(7) J. W. Cornforth in *The Chemistry of Penicillin*, Princeton University Press, Princeton, N. J., 1949, p. 735.

(8) (a) R. Filler and J. D. Wismar, *J. Org. Chem.* **22**, 853 (1957). (b) A. Mustafa and A. H. E. Harhash, *J. Org. Chem.* **21**, 575 (1956).

(9) Melting points were determined on a Fisher-Johns block and are not corrected.

8-(2-Methoxyethoxy)caffeine

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Kihlman[1] has reported. that 8-ethoxycaffeine produced structural chromosomal changes in the root tips. This and closely related compounds have been studied at the Roswell Park Memorial Institute as possible anti-cancer agents. 8-(2-Methoxyethoxy)caffeine was prepared from 8-chlorocaffeine and sodium 2-methoxyethoxide by the general method of Huston and Allen.[2] The crude product, obtained in 80% yield, was recrystallized twice from hot water and once from carbon tetrachloride; m.p. 98.5–99.5° (Fisher-Johns melting

(1) B. Kihlman, *Exptl. Cell Research* 1, 135 (1950).

(2) R. C. Huston and W. F. Allen, *J. Am. Chem. Soc.*, **56**, 1356 (1934).