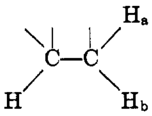
lation was treated with boiling ether and filtered. Cooling of the concentrated filtrate to −16°, filtration, and recrystallization from ether and cyclohexane gave 13.2 g (11% of theory) of pure 2,2-dimethyl-6-(trichloromethyl)tetrahydro-1,4-pyrone (III): mp 79–81°; ν_{max}^{Nujol} 2900, 1725, 1465, 1380, 1315, 1280, 1255, 1205, 1125, 1095, 970, 895, 870, 855, 820, 770, and 670 cm^{-1}; nmr, $\nu_{max}^{CCl_4}$, 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: ν_{max}^{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.

Acknowledgments.—This work was supported by fellowship grants from Celanese Corporation of America and from Harris Research Laboratories, Washington, D. C., to one of the authors (E. K.), and this support is gratefully acknowledged. The assistance of Mrs. Helen Sing and Dr. William McFarlane in interpreting the nmr spectra is deeply appreciated.

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

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Received September 14, 1965

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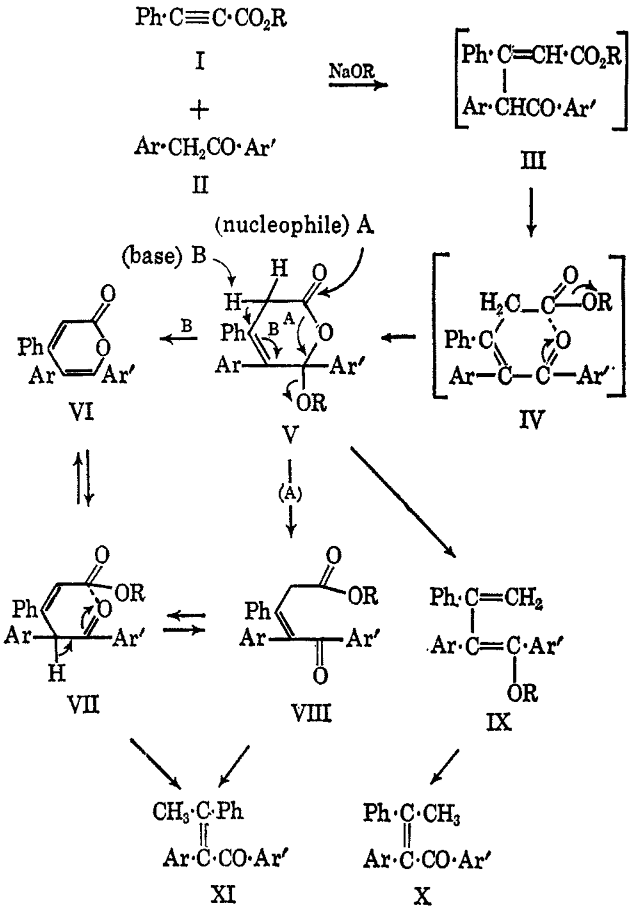
[1] Part VI: I. El-Sayed El-Kholy, M. M. Mishrikey, F. K. Rafla, and G. Soliman, *J. Chem. Soc.*, 5153 (1962).

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

SCHEME I



Compd	Ar	Ar′
a	Ph	Ph
b	Ph	p-MeO·C$_6$H$_4$
c	p-MeOC$_6$H$_4$	p-MeO·C$_6$H$_4$
d	Ph	p-MeS·C$_6$H$_4$
e	Ph	p-Me·C$_6$H$_4$
f	Ph	p-Br·C$_6$H$_4$

considered to arise by a shift of the double bond in VIIa,b.

In contrast to the two latter groups of esters VII and VIII with respect to their thermal stability and susceptibility to pyrone formation with sodium ethoxide in ether, the previously supposed *trans* esters IIIa–c (R = Et) are thermolabile and readily give the esters VIII and/or the pyrones VI on acid-catalyzed alcoholysis (*cf.* Experimental Section).

This behavior led us to prepare new intermediate methyl and ethyl esters by condensation of a variety of deoxybenzoins IIa–f with methyl and ethyl phenylpropiolate I (R = Me or Et) in the presence of sodium methoxide and ethoxide, respectively. This provided a secure foundation for the differentiation among the three groups of esters and for the interpretation of the formation of the thermolabile esters.

We have confirmed by infrared determination the structures assigned to the normal δ-keto esters VIIa (R = Me) and VIIIa (R = Me) on the basis of ozonolysis results.[2a] The infrared spectral data (see Table I) for methyl 5-oxo-3,4,5-triarylpent-2-enoates (VIIa–c) show two strong absorption bands (columns A and B) of which the former is attributable to the α,β-unsaturated ester carbonyl[3a] and the latter to the aroyl carbonyl group[3b] which are separated by *ca.* 60 cm^{-1}. The isomeric Δ^3 esters VIIIa,b exhibit the normal ester carbonyl and the α,β-unsaturated aroyl carbonyl bands[3a,b] (A and B) which are separated by *ca.* 80 cm^{-1}.

TABLE I

INFRARED ESTER AND KETONE CARBONYL CHARACTERISTICS OF THE ψ ESTERS V, δ-KETO ESTERS VII AND VIII, AND THE α,β-UNSATURATED KETONES X AND XI

Compd	R	A, C=O (s)	B, C=O (s)
ψ esters			
Va	Et	1742	. . .
Va	Me	1742	. . .
Vb	Et	1729	. . .
Vb	Me	1724	. . .
Vc	Et	1721	. . .
Vc	Me	1727	. . .
Δ^2-Keto esters			
VIIa	Me	1724	1667
VIIb	Me	1721	1653
VIIc	Me	1721	1658
Δ^3-Keto esters			
VIIIa	Me	1739	1658
VIIIa	Et	1739	1661
VIIIb	Me	1727	1645
Ketones			
Xa	. . .	. . .	1658
Xb	. . .	. . .	1650
XIa	. . .	. . .	1650
XIb	. . .	. . .	1653

On the other hand, the infrared spectra of both the previously considered *trans* esters Va–c (R = Et) and the newly prepared esters Va–f (R = Me or Et) show only one carbonyl band (A) of δ-lactones[3c,4] which appear almost in the same position as in the corresponding isomeric open-chain methyl or ethyl Δ^3 esters VIII indicating β,γ unsaturation. Obviously, the absence of the aroyl carbonyl band in the spectra of these esters indicates their cyclic structure and distinguishes them from the normal δ-keto esters VII and VIII.

The ultraviolet spectrum of the ψ ester (Va, R = Et) showed only a plateau at 250–260 mμ (log ε 4.01) which is different from the normal δ-keto esters VIIa and VIIIa (R = Me) which absorb at 248 mμ (log ε 4.32) and 253 mμ (log ε 4.36), respectively. Moreover, the β,γ unsaturation of the ψ esters V was confirmed by nmr study of 4,5,6-triphenyl-6-ethoxy-2-oxo-3,6-dihydropyran (Va, R = Et) in deuteriochloroform. The spectrum contained four groups of peaks: the methyl group of the ethoxyl at 6 position appeared as a triplet at δ = 1.1 ppm with coupling constant J = 7 cps; the methylene group of the same ethoxyl appeared as a quadruplet at δ = 3.65 ppm with coupling constant J = 7 cps; the methylene group of the heterocyclic ring (position 3) appeared as a singlet at δ = 3.61 ppm; and the phenyl groups appeared at *ca.* δ = 7.1 ppm. The absence of the CH absorption (position 5) in the spectrum of this ψ ester excludes the α,β unsaturation.

Although the formation and peculiar properties of the five-membered ψ esters obtained from *cis*-β-aroyl-α- and β-methyl acrylic acids,[5] *o*-formyl-, *o*-acetyl-, and *o*-

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[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1959: (a) p 179; (b) p 132; (c) p 185; (d) p 34.

[4] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

[5] R. E. Lutz, P. S. Bailey, C. K. Dien, and J. W. Rinker, *J. Am. Chem. Soc.*, **75**, 5039 (1953); R. E. Lutz, C. T. Clark, and J. P. Feifer, *J. Org. Chem.*, **25**, 346 (1960).

benzoylbenzoic acids[4,6,7] were extensively studied, our six-membered ψ esters V appear to be unprecedented in literature.

We suggest, however, that these ψ esters arise from such primary intermediate adducts as the *cis* esters of III by shift of the double bond. Subsequently, the resulting *cis*-5-oxo-3,4,5-triarylpent-3-enoates (IV, R = Me or Et) are probably attacked on the aroyl carbon by the alkoxide ion with cyclization to the ψ esters V and elimination of the ester alkoxyl. These ψ esters, without ring opening, can by elimination of alcohol (alkoxide), proceed to the pyrones VI (path B).

The δ-lactol ester structure of these ψ esters accounts for the ease of their transformation to a mixture of the 5-oxo-3,4,5-triarylpent-3-enoic esters (VIII) and the pyrones VI in acid-catalyzed alcoholic media and in some cases, the pyrone was the sole product. The formation of the normal δ-keto esters VIII takes place by acid-catalyzed protonation of the ether oxygen and fission of the bond between the carbonyl carbon and the ether oxygen (path A). However, the pyrone formation involves a shift in the position of the double bond and elimination of R·OH. On the other hand, the normal δ-keto esters VII and VIII remain intact in such a medium, but would undergo transesterification.

Whereas, the ψ esters of *o*-benzoylbenzoic acid give varying yields of the normal methyl esters in methanol containing methoxide ion,[6a,8] our ψ esters V are partly converted into the pyrones VI after brief treatment with this reagent. However, the normal δ-keto esters VII of VIII under such conditions immediately gave the pyrones VI. Likewise, the β,γ-unsaturated lactonic structure of these ψ esters V accounts for the elimination of carbon dioxide on heating at their melting points. Moreover, the pyrolysis products IXa (R = Et) and IXb (R = Me or Et) which have been obtained pure, were shown to be alkali stable. Their analyses, degradation, and infrared study indicate that they are 1-alkoxy-1,2,3-triarylbutadienes.

The position of the alkoxyl group with respect to the three aryl groups in IXa (R = Et) and IXb (R = Me or Et) was established by autoxidation and ozonolysis of the former to benzil and ethyl benzoate and ozonolysis of the latter to benzil and ethyl anisate. The infrared spectra of these butadiene ethers are characterized by the out-of-plane band at 902–908 cm^{-1} and the overtone band at 1880 cm^{-1} associated with the exomethylene group.[3d] Being α,β-unsaturated ethers, the butadienes IXa (R = Et) and IXb (R = Me or Et) were easily converted to the corresponding α,β-unsaturated ketones Xa,b by acid-catalyzed hydrolysis. The resulting ketones are probably the *trans* isomers of the ketones XIa,b previously obtained[2a] by pyrolysis of the acids VIIa,b (R = H) or VIIIa,b (R = H). The two pairs of ketones exhibit strong absorption in the region 1650–1658 cm^{-1} characteristic of α,β-unsaturated ketones.[3b] Further, ozonolysis of the ketones Xa and XIa led to the isolation of acetophenone, benzil, and benzoic acid, indicating that they have identical skeletal structure. Determination of the structure of these isomers is currently under investigation.

Experimental Section[9]

4,5,6-Triphenyl-6-methoxy-2-oxo-3,6-dihydropyran (Va, R = Me).—Methyl phenylpropiolate (3.3 g) and deoxybenzoin (4 g) were condensed with sodium methoxide (1.2 g) in ether for 2 days at room temperature. Isolation by a standard procedure[2a] yielded 4,5,6-triphenyl-2-pyrone (VIa) (1.95 g, 33%) and an enolic fraction (4.2 g) from which the ψ ester (Va, R = Me), 2.7 g, mp 112–115° (dec), was obtained in 37% yield on treatment with cold methanol. It crystallized from benzene–petroleum ether in needles, mp 120° (dec).

Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.87; H, 5.66; OMe, 8.70. Found: C, 80.89; H, 5.86; OMe, 8.50.

A solution of this ψ ester (0.2 g) in methanol (15 ml) containing 2 drops of concentrated hydrochloric acid yielded on spontaneous evaporation methyl 5-oxo-3,4,5-triphenylpent-3-enoate[2a] (VIIIa, R = Me; 0.15 g), mp and mmp 107°, and traces of the pyrone VIa.

Ethyl 5-Oxo-3,4,5-triphenylpent-3-enoate (VIIIa, R = Et).—A solution of the ψ methyl or ψ-ethyl ester[2a] Va (R = Me or Et) in ethanol acidified with few drops concentrated hydrochloric acid was evaporated or refluxed for 20 min. The ester VIIIa (R = Et) was crystallized from methanol in needles, mp 101°.

Anal. Calcd for $C_{25}H_{22}O_3$: C, 81.04; H, 5.99; OEt, 12.16. Found: C, 80.60; H, 5.65; OEt, 11.68.

Transesterification.—Ethyl 5-oxo-3,4,5-triphenylpent-3-enoate (VIIIa, R = Et) (0.2 g) was refluxed with 3 drops of concentrated hydrochloric acid in methanol (25 ml) for 3 hr; the methyl ester VIIIa (R = Me) (0.15 g), mp and mmp 107°, was obtained by evaporation and crystallization.

Ethyl 5-oxo-3,4,5-triphenylpent-2-enoate (VIIa, R = Et) was also converted into the methyl ester VIIa (R = Me), mp and mmp 130°, on similar treatment.

Action of Sodium Methoxide on the ψ Esters.—A solution of 0.7 g of the ψ-ethyl ester Va (R = Et), 0.12 g of sodium methoxide (from 0.05 g of sodium) in absolute methanol became yellow and 4,5,6-triphenyl-2-pyrone (VIa) (0.2 g, 33%) was separated immediately. The filtrate was diluted with ice-cold water and extracted with ether, and the alkaline solution was acidified with 10% sulphuric acid and extracted with ether. The latter ethereal solution was shaken with 2% sodium hydrogen carbonate solution, dried, and distilled to give 0.3 g (42%) of unchanged ψ-ethyl ester Va (R = Et).

The ψ-ethyl ester Vb (R = Et) (0.5 g) when treated as described before gave 0.15 g of 4,5-diphenyl-6-*p*-methoxyphenyl-2-pyrone (VIb) besides the unchanged ψ ester.

4,5-Diphenyl-6-*p*-methoxyphenyl-6-methoxy-2-oxo-3,6-dihydropyran (Vb, R = Me).—Condensation of 3 g of methyl phenylpropiolate, 4.2 g of 4′-methoxydeoxybenzoin, and 1.1 g of sodium methoxide in dry ether, gave 1.5 g (23%) of 4,5-diphenyl-6-*p*-methoxyphenyl-2-pyrone (VIb)[2a] and 3.9 g of enolic fraction from which 2.7 g (37.5%) ψ-methyl ester Vb (R = Me) was obtained on treatment with benzene–petroleum ether. It crystallized from methanol in prisms, mp 127°(dec).

Anal. Calcd for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74; 2OMe, 16.06. Found: C, 77.81; H, 5.93; OMe, 15.88.

A solution of this ψ-methyl ester in methanol containing 2 drops of concentrated hydrochloric acid produced on evaporation methyl 5-oxo-3,4-diphenyl-5-*p*-methoxyphenylpent-3-enoate[2a] (VIIIb, R = Me), mp and mmp 113°, and traces of the pyrone VIb.

5,6-Di-*p*-methoxyphenyl-4-phenyl-6-methoxy-2-oxo-3,6-dihydropyran (Vc, R = Me).—Condensation of 3.3 g of methyl phenylpropiolate, 5.3 g of 4,4′-dimethoxydeoxybenzoin, and 1.2 g of sodium methoxide in ether yielded 2.9 g (36.6%) of 5,6-di-*p*-methoxyphenyl-4-phenyl-2-pyrone (VIc)[2a] and 2.2 g (25.5%) of the ψ-methyl ester Vc (R = Me). It crystallized from benzene–petroleum ether in prisms, mp 147° (dec).

Anal. Calcd for $C_{26}H_{24}O_5$: C, 74.98; H, 5.81; 3OMe, 22.36. Found: C, 75.31; H, 5.94; OMe, 22.69.

A solution of this ψ-methyl ester or the analogous ψ-ethyl ester Vc (R = Et)[2a] in methanol containing 2 drops of concentrated hydrochloric acid gave exclusively the pyrone VIc on evaporation at room temperature.

Methyl 5-Oxo-4,5-di-*p*-methoxyphenyl-3-phenylpent-2-enoate (VIIc, R = Me).—The corresponding acid VIIc (R = H) was

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(6) (a) M. S. Newman, *et al.*, *J. Am. Chem. Soc.*, **67**, 253 (1945); (b) *ibid.*, **84**, 3582 (1962).

(7) W. A. Bonner, *ibid.*, **85**, 439 (1963).

(8) R. Filler and L. M. Hebron, *ibid.*, **81**, 391 (1959).

(9) Melting points are uncorrected. Elemental analyses were by Alfred Bernhardt Laboratories, West Germany. The petroleum ether used had bp 50–70°. Infrared spectra (cm^{-1}) were measured on Perkin-Elmer 137 spectrophotometer for KBr pellets.

obtained by fission of the pyrone VIc with methanolic potassium hydroxide and crystallized from benzene in needles, mp 166–167°(dec).

Anal. Calcd. for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51; 2OMe, 15.43. Found: C, 74.69; H, 5.56; OMe, 15.25.

The methyl ester VIIc (R = Me) was prepared by diazomethane and crystallized from methanol in prismatic needles, mp 120°.

Anal. Calcd for $C_{26}H_{24}O_5$: C, 74.98; H, 5.81; 3 OMe, 22.36. Found: C, 75.11; H, 5.78; OMe, 22.49.

This ester was converted to the pyrone VIc when its ethereal solution was treated with sodium methoxide.

The methyl esters VIIa,b (R = Me) were recovered unchanged after being refluxed in methanol containing few drops of concentrated hydrochloric acid for 2 hr.

The ψ-methyl esters Vd-f (R = Me) and their ψ-ethyl analogs Vd–f (R = Et) were prepared besides the corresponding 2-pyrones VId–f and the results of their investigation will be reported in a subsequent publication.

1-Ethoxy-1,2,3-triphenylbuta-1,3-diene (IXa, R = Et).—The ψ-ethyl ester Va (R = Et) (1 g) was heated just above its melting point and kept at 135° until carbon dioxide ceased to evolve. After cooling, the viscous residue was boiled with petroleum ether and the traces of the pyrone VIa were separated. Concentration of the petroleum ether extract and cooling gave 0.4 g (45%) of the diene IXa (R = Et) which crystallized from methanol in cubes, mp 75°.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.28; H, 6.80; OEt, 13.80. Found: C, 88.06; H, 7.09; OEt, 14.00.

Autoxidation of the Diene IXa (R = Et).—The diene IXa (R = Et) (1 g) was kept for a long time. It gradually lost its crystalline shape and was transformed into a viscous brown oil contaminated with crystals of benzil. On treatment with cold petroleum ether, benzil, mp and mmp 95°, was separated and the solution contained ethyl benzoate. It was identified by acid hydrolysis to benzoic acid.

Ozonolysis of the Diene IXa (R = Et).—A solution of 0.9 g of the diene IXa (R = Et) in chloroform was subjected to ozonized oxygen and the solvent was distilled. The ozonide was decomposed by water and extracted with ether. The ethereal solution was shaken with sodium hydrogen carbonate and the neutral solution was evaporated to give benzil and ethyl benzoate (identified as before). The acidic product obtained by acidification of the sodium hydrogen carbonate solution gave benzoic acid on treatment with petroleum ether.

1-Ethoxy-2,3-diphenyl-1-*p*-methoxyphenylbuta-1,3-diene (IXb, R = Et).—Heating 1 g of the ψ-ethyl ester Vb (R = Et) at *ca.* 150° until carbon dioxide ceased to evolve gave traces of the pyrone VIb and 0.35 g (39%) of the diene IXb (R = Et). The diene crystallized from petroleum ether in plates, mp 85°.

Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.26; H, 6.76; OMe, 8.71; OEt, 12.65. Found: C, 84.12; H, 6.89; OMe, 8.19; OEt, 11.90.

1-Methoxy-2,3-diphenyl-1-*p*-methoxyphenylbuta-1,3-diene (IXb, R = Me).—Heating 0.5 g of the ψ-methyl ester Vb (R = Me) at *ca.* 135° gave 0.35 g (76%) of the diene IXb (R = Me). It crystallized from methanol in prisms, mp 107°.

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48; 2 OMe, 18.13. Found: C, 83.73; H, 6.24; OMe, 17.94.

The ethers IXa (R = Et) and IXb (R = Et or Me) were recovered unchanged after heating with methanolic potassium hydroxide for 1 hr.

Ozonolysis of the Diene IXb (R = Et).—The diene IXb (R = Et) (0.5 g) was subjected to ozonolysis and work-up as for IXa (R = Et) gave 0.3 g of acidic fraction from which 0.2 g of benzoic acid and traces of anisic acid were separated. The neutral fraction contained traces of benzil (separated by steam distillation) and ethyl anisate identified by acid hydrolysis to anisic acid.

***trans*-(?)-1-Oxo-1,2,3-triphenylbut-2-ene (Xa).**—A solution of 0.5 g of the butadiene IXa (R = Et) in methanol was refluxed with 3 drops of concentrated hydrochloric acid or sulphuric acid for 20 min. On concentration, dilution, and extraction with ether, 0.45 g (100%) of the ketone Xa was recovered. It crystallized from methanol in needles, mp 101°, which failed to give an oxime.

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.33; H, 5.95.

Ozonolysis of the Ketone Xa.—A solution of 0.78 g of the ketone Xa in chloroform was ozonized at 0°. After decomposition of the ozonide, the residue was subjected to steam distillation. The distillate (800 ml) which contained a yellow solid and oily droplets was extracted with ether. The oily residue (0.55 g) recovered from the ethereal solution gave benzil, mp and mmp 95°, on crystallization from petroleum ether. The residual oil recovered from petroleum ether mother liquor gave a mixed 2,4-dinitrophenylhydrazone from which benzil-2,4-dinitrophenylhydrazone was recovered by boiling ethanol. The insoluble portion was crystallized from glacial acetic acid in red needles, mp 248–50°, identical with acetophenone 2,4-dinitrophenylhydrazone. The same ozonolysis products were also obtained from the isomeric ketone XIa.

***trans*-(?)-1-Oxo-2,3-diphenyl-1-*p*-methoxyphenylbut-2-ene (Xb).**—A solution of 0.7 g of the butadiene IXb (R = Me) or IXb (R = Et) in methanol was refluxed with 3 drops of concentrated hydrochloric acid for 30 min to give 0.5 g (75%) of the ketone Xb. It crystallized from methanol in needles, mp 117°, which failed to give an oxime.

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.10; H, 6.15; OMe, 9.45. Found: C, 84.18; H, 6.24; OMe, 9.37.

Acknowledgment.—We wish to thank Dr. G. Soliman, Professor of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Khartoum, for his keen interest in this subject and for many stimulating discussions. Also, we thank Mr. Richard Gilespy, Instrumentation, Chemistry Department, University of California, Los Angeles, California, for doing the nmr spectrum.