linoleate "the debrominated material contained large amounts of positional and geometric isomers and less than 75% of the 9,12-di-*cis*-octadecadienoic acid."

In conclusion it should be said that although the method may be used in some cases to determine whether one or more double bonds in a molecule are *cis* or *trans*, it could not, of course, from length measurements alone locate the position of these double bonds. The solution of such a problem would depend on an evaluation of the intensities of the continuous lines in the X-ray photographs. The applicability of line intensities for the problem of locating the position of functional groups has already been demonstrated.[25]

Acknowledgment.—The authors wish to acknowledge gratefully the assistance of Dr. K. C. Peng who took many of the X-ray photographs used in the work.

(25) N. Nicolaides, F. Laves and A. Niggli, THIS JOURNAL, **78**, 6415 (1956).

ZÜRICH, SWITZERLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Experiments in the Colchicine Field. V. The Thermal and Photochemical Decomposition of Various 2-(β-Phenylethyl)-phenyldiazomethanes and 2-(γ-Phenylpropyl)-phenyldiazomethanes[1]

BY C. DAVID GUTSCHE, EMIL F. JASON,[2] ROBERT S. COFFEY[3] AND HERBERT E. JOHNSON

RECEIVED MAY 28, 1958

For an investigation of reactions leading to tricyclic cycloheptatriene compounds, 2-[β-(4′-methoxyphenyl)-ethyl]-phenyldiazomethane, 2-(γ-phenylpropyl)-phenyldiazomethane, 2-[γ-(4′-methoxyphenyl)-propyl]-3,4,5-trimethoxyphenyldiazomethane and 2-[γ-(3′,4′-dimethoxyphenyl)-propyl]-3,4,5-trimethoxyphenyldiazomethane have been prepared and subjected to thermal and/or photochemical decomposition. From the first two diazo alkanes small amounts of tricyclic cycloheptatriene may be formed, but no evidence for this type of compound is found in the products from the second two diazo alkanes. In all cases, the major cyclic material is the indan and/or tetralin resulting from attack at a point on the polymethylene bridge between the aromatic nuclei. The decomposition of 2-(γ-phenylpropyl)-phenyldiazomethane was studied in detail, and the products have been shown to include 2-phenyltetralin, 2-benzylindan, 2-(γ-phenylpropyl)-benzaldehyde, 2-(γ-phenylpropyl)-benzonitrile and 2-(γ-phenylpropyl)-benzal azine. The indan/tetralin ratio was studied as a function of reaction conditions and was found to be temperature dependent. Independent syntheses for the indans and tetralins are described.

An intramolecular counterpart of the reaction of phenyldiazomethane with benzene to form phenylcycloheptatriene (*cf.* Experimental) involves the decomposition of 2-(β-phenylethyl)-phenyldiazomethane (I) to 6,6a-dihydro-5*H*-cyclohepta[a]-naphthalene (VI) and 2-phenylindan (VIII) as reported in the previous paper of this series.[4] In the hope of extending this procedure to the synthesis of compounds related to colchicine a variety of 2-(β-phenylethyl)-phenyldiazomethanes and 2-(γ-phenylpropyl)-phenyldiazomethanes have been prepared and decomposed. Although the results are singularly disappointing from the standpoint of a colchicine synthesis, they have some pertinence to the currently expanding field of carbene chemistry and are, therefore, reported in detail.

Thermal and Photochemical Decomposition of 2-(Arylalkyl)-phenyldiazomethanes.—The formation of the tricyclic cycloheptatriene (VI) from the irradiation of the diazo compound I gave encouragement that a similar reaction with the diazo compounds IV and V might lead to substances closely resembling colchicine. This hope was abetted by a consideration of the probable mechanism for the reaction. Considerable data have accumulated which suggest that the initial action of heat or light on a diazoalkane is to release molecular nitrogen and produce a fragment which has been designated as a "carbene."[5] A carbene might be expected to be electrophilic and as a consequence to react with centers of highest electron density.[6] Thus, a compound of the type IV would be predicted to form a tricyclic cycloheptatriene more readily than an unmethoxylated analog. In actual fact, however, the photochemical decomposition of IV in dilute petroleum ether solution at 65° or the thermal decomposition at 175° yielded a mixture which showed no spectral evidence for this type of substance. Instead, the products included the aldehyde XXXIV, the nitrile XVI, the azine and the tetralin XII. Similarly, the photochemical decomposition of V under comparable conditions yielded no spectrally detectable tricyclic cycloheptatriene derivative but instead produced the aldehyde XXXV, the nitrile XVII, the azine and the tetralin XIII.

Further study of the reaction was carried out with the diazo compounds II and III, the first to test more definitely the effect of a methoxyl group and the second to test the effect of the length of the bridge between the two aryl groups. When II was subjected to photochemical decomposition in dilute petroleum ether solution at 65° an amount of tricyclic cycloheptatriene (VII) was formed which was equal to or smaller than the amount of

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(1) This work was supported, in part, by grants-in-aid from: (a) The Office of Ordnance Research, U. S. Army (Contract No. DA-23-072-ORD-592); (b) The National Science Foundation.

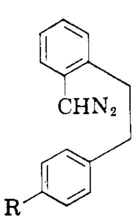
(2) Charles F. Kettering Fellow, 1956–1957.

(3) Postdoctoral Research Associate, 1957–1958.

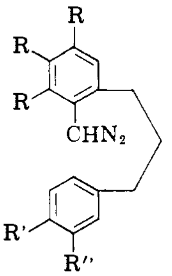
(4) C. D. Gutsche and H. E. Johnson, THIS JOURNAL, **77**, 5933 (1955).

(5) For a definition of "carbene" *cf.* W. von E. Doering and L. H. Knox, *ibid.*, **78**, 4947 (1956), footnote 9.

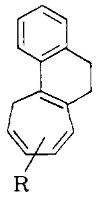
(6) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. E. Parham and C. D. Wright, *J. Org. Chem.*, **22**, 147 (1957); and P. S. Skell and R. M. Etter, *Chemistry & Industry*, 624 (1958), have adduced data in support of the electrophilic character of dihalocarbenes and carbethoxycarbene. The degree of similarity between these and alkyl- or arylcarbenes, however, has not been delineated.



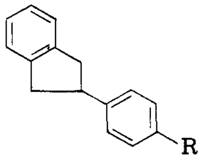
I, R = H
II, R = CH_3O



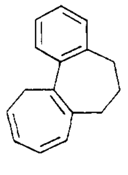
III, R = R' = R'' = H
IV, R = R' = CH_3O, R'' = H
V, R = R' = R'' = CH_3O



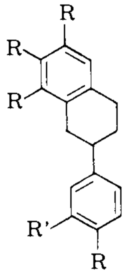
VI, R = H
VII, R = CH_3O



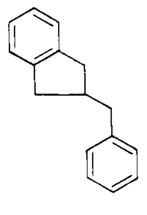
VIII, R = H
IX, R = CH_3O



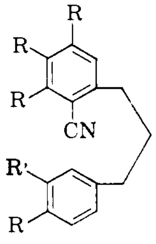
X



XI, R = R' = H
XII, R = CH_3O, R' = H
XIII, R = R' = CH_3O



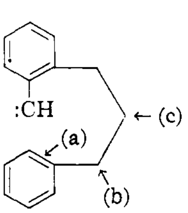
XIV



XV, R = R' = H
XVI, R = CH_3O, R' = H
XVII, R = R' = CH_3O

VI formed from I under comparable conditions. Thus, the lack of influence by the methoxyl group is further substantiated.[7] As in the case of I where the major product was 2-phenylindan (VIII), the major product from this reaction was 2-(*p*-methoxyphenyl)-indan (IX).

The decomposition of 2-(γ-phenylpropyl)-phenyldiazomethane (III) was carried out under a variety of conditions. The products formed included 2-phenyltetralin (XI), 2-benzylindan (XIV), 2-(γ-phenylpropyl)-benzonitrile (XV), 2-(γ-phenylpropyl)-benzaldehyde (XXXIII) and 2-(γ-phenylpropyl)-benzalazine.[8] Efforts to isolate the tricyclic cycloheptatriene (X) from the reaction mixture were without success. By means of distillation and column chromatography on alumina it was possible to separate an oil in 4.5% yield which is thought, on the basis of an ultraviolet absorption band at 235 mμ, to contain *ca.* 10% of X. Further purification or removal of X as a maleic anhydride adduct failed, however. The only cyclic products isolated were 2-phenyltetralin (XI) and 2-benzylindan (XIV). The combined yield of these materials amounted to 15–25% with the relative proportions differing somewhat depending upon the reaction conditions; irradiation at 15–18° gave an apparent indan/tetralin ratio of 9:1 as determined by vapor phase chromatography, irradiation at 65° a ratio of 6:1, and purely thermal decomposition at 175° a ratio of 2:1. While no precise significance should be attached to these data, it does appear that the ratio is temperature sensitive in contrast with earlier observations for the reaction of diazomethane with hydrocarbons and olefins.[9] In addition to observing no temperature dependence, Doering and coworkers also found that diazomethane shows little if any discriminatory power with respect to types of carbon–hydrogen bonds and only a sixfold preference for a double bond over a carbon–hydrogen bond. In the present case there is superimposed on the features of previously-studied systems an additional factor, *viz.*, the proximity of the diazo group to the group with which it reacts. Thus the presumably greater inherent tendency for an aromatic ring (point a) to interact with a carbene[10] might, in the case of III (*cf.* structure XVIIIa), be more than offset by the distance between the aromatic ring and the carbene. As a result, reaction at points b and c would take precedence with c favored over b. A possible explanation for the temperature dependence of the ratio of attack at c and b (indan/tetralin ratio) rests on the postulate that the nitrogen-free intermediate may have some



XVIIIa

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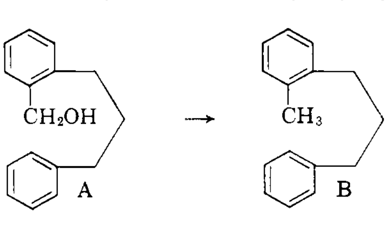
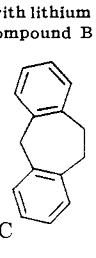
(7) H. Meerwein, H. Disselnkötter, F. Rappen, H. v. Rintelen and H. van de Vloed, *Ann.*, **604**, 151 (1957), have stated that diazomethane reacts, under irradiation conditions, with approximately equal facility with benzene, chlorobenzene and anisole.

(8) Also isolated from one of the reaction mixtures was 2-(γ-phenylpropyl)-toluene (compound B). It, however, is not considered to be a photolysis product but is thought to arise from the hydrazone in a Wolff–Kishner type of reduction. An authentic sample was prepared by reducing the acid XXIV to the corresponding alcohol A with lithium aluminum hydride and then catalytic hydrogenolysis to compound B



A B



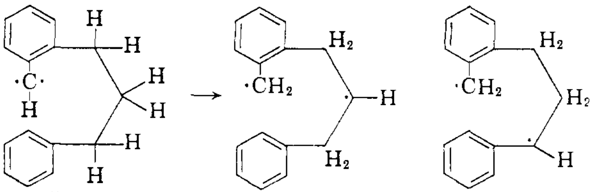
C

Another plausible product from the reaction would be 1,2,4,5-dibenzocycloöctadiene (compound C). A sample of this was prepared in very poor yield by cyclization of XXIV and subsequent Wolff–Kishner reduction of the resulting ketone. A diacetyl derivative was obtained as a liquid from which a solid 2,4-dinitrophenylhydrazone was prepared. Although our experimental data are inconclusive in this regard, it is felt that C is probably not a significant component of the reaction mixture.

(9) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N., Chaudhuri, THIS JOURNAL, **78**, 3224 (1956) [*cf.* ref. 11, footnote 16, for a correction to one of the results reported in this paper].

(10) The many reactions of diazoacetic ester with aromatic compounds to form norcaradiene and cycloheptatriene derivatives [*cf.* M. Gordon, *Chem. Revs.*, **50**, 127 (1952)] as well as a number of more recent observations with various diazoalkanes and diazoketones [*cf.* W. Treibs, M. Quarg and E. J. Poppe, *Ann.*, **598**, 32 (1956), for a list of references] support, in general, the proposition that the aromatic ring is more reactive to diazoalkanes than is the carbon–hydrogen bond.

biradical character[11,12] and that reactions involving the biradical (XVIIIb) are more strongly temperature dependent than those involving the carbene.[13] Thus, the indan and tetralin could arise through carbene (XVIIIa) attack at c or b *or* through transfer of a hydrogen atom from c or b of the *gem*-biradical XVIIIb to form a new biradical (XIX or XX), electron pairing then leading to XI and XIV.



XVIIIb XIX XX

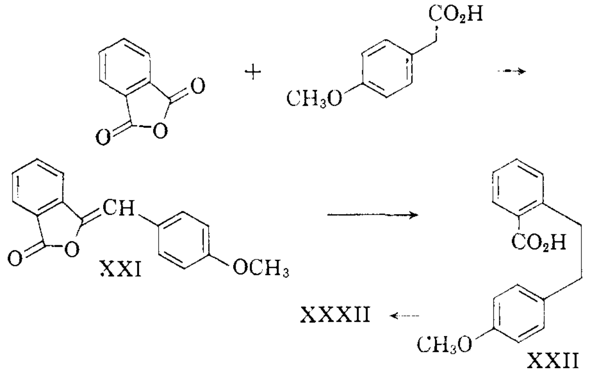
To the extent that the latter route is followed it might be assumed that the tetralin would be the preferred product, for biradical XX would be predicted to be more stable than biradical XIX.

The 2-(γ-phenylpropyl)-benzaldehyde (XXXIII) isolated from many of the decomposition reaction mixtures was shown to arise from the diazo compound III. When a sample of III free from aldehyde (as indicated by the absence of carbonyl absorption in the infrared spectrum) was dissolved in petroleum ether and refluxed in the presence of air, extensive conversion to the aldehyde occurred. A comparable experiment carried out in an atmosphere of nitrogen showed little, if any, formation of aldehyde. It is interesting to note that the rate of disappearance of diazo compound is considerably greater in the presence of oxygen suggesting that (a) the reaction with oxygen does not involve a carbene or (b) oxygen accelerates the formation of the carbene. The reaction with oxygen to form the aldehyde appears to be catalyzed by the metals (*e.g.*, mercury or silver) formed in the preparation of the diazo compounds (through oxidation of the hydrazones). Consequently, it is important not to prolong the hydrazone oxidation, to remove the precipitated metals as efficiently as possible, to protect the diazo compound from the air, and to use the diazo compound as soon after preparation as possible. To minimize aldehyde formation most of the decompositions were carried out in an atmosphere of nitrogen.

Certain unidentified materials in some of the reaction mixtures probably have their genesis in the aldehyde which arises as indicated. In the reaction mixtures from decompositions carried out in the presence of air, the infrared spectrum invariably contained bands at 1710 and 1770 cm.$^{-1}$, these bands being very weak or missing in the products from decompositions carried out under nitrogen. That these bands arise from conversion products of the aldehyde is suggested by an experiment in which the aldehyde XXXV was subjected to the conditions of irradiation used in the photolysis reactions. The original infrared absorption band at 1695 cm.$^{-1}$ (aldehyde carbonyl) disappeared almost completely and was replaced by strong bands at 1710 and 1760 cm.$^{-1}$. The identity of the substance(s) was not established, although in a comparable experiment with benzaldehyde, one of the products was shown to be hydrobenzoin, isolated in 35% yield.[14]

The nitrile found in some of the reaction mixtures appears also to arise from the diazo compound, for a sample of the hydrazone from XXXIII (free of nitrile as indicated by the absence of an absorption band at 2230 cm.$^{-1}$) did not yield any nitrile when irradiated and refluxed in petroleum ether for several days.

Synthesis of 2-(Arylalkyl)-phenyldiazomethanes.—In all instances the procedure of Staudinger and Gaule[15] was employed for the preparation of the diazo compound. This method, involving the conversion of the aldehyde to the corresponding hydrazone followed by oxidation (*e.g.*, with mercuric oxide), required the appropriate aldehyde as starting material. In the case of 2-[β-(*p*-methoxyphenyl)-ethyl]-benzaldehyde (XXXII) the synthesis involved, as the initial step, the condensation of phthalic anhydride with *p*-methoxyphenylacetic acid to give *p*-methoxybenzal phthalide (XXI) in 82% yield. Reduction to *p*-methoxybenzyl phthalide, cleavage of the lactone ring with potassium hydroxide and further hydrogenation yielded 2-[β-(*p*-methoxyphenyl)-ethyl]-benzoic acid (XXII) in 82% over-all yield. Reduction of the acid to the corresponding aldehyde XXXII was effected in 38% yield by the Sonn–Müller method.[16] Compounds of the 2-(γ-arylpropyl)-benzaldehyde series were prepared *via* chalcone intermediates resulting from the condensation of substituted benzaldehydes with substituted acetophenones. For the synthesis of 2-(γ-phenylpropyl)-benzaldehyde (XXXIII) the starting material was benzal-2-carboxyacetophenone, obtained from benzaldehyde and 2-carboxyacetophenone in 98% yield. Catalytic reduction of the chalcone to the saturated ketone, thermal conversion to the corresponding enol lactone XXIII, and treatment with phosphorus and hydrogen iodide provided 2-(γ-phenylpropyl)-benzoic acid (XXIV) in *ca.* 50%



XXI XXII XXXII

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(11) H. M. Frey and G. B. Kistiakowsky, THIS JOURNAL, **79**, 6373 (1957).

(12) G. A. Gallup, *J. Chem. Phys.*, **26**, 716 (1957).

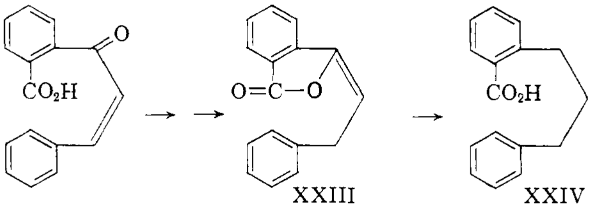
(13) J. Chanmugam and M. Burton, THIS JOURNAL, **78**, 509 (1956), have provided evidence in support of this postulate in a study of the photolysis of ketene in the presence of hydrogen and deuterium.

(14) C. Ciamician and P. Silber, *Ber.*, **36**, 1575 (1903), showed that the irradiation of benzaldehyde gave a mixture of hydrobenzoin, benzoic acid and a polymer represented as $(C_7H_6O)_9$.

(15) F. Staudinger and A. Gaule, *ibid.*, **49**, 1897 (1916).

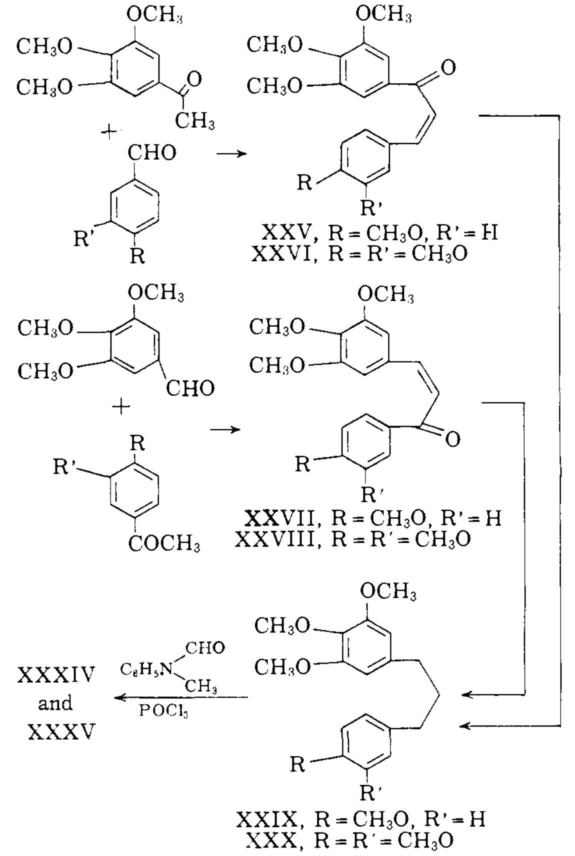
(16) A. Sonn and E. Müller, *ibid.*, **52**, 1927 (1919).

over-all yield from the chalcone.[17] Reduction to the aldehyde was effected by the Sonn–Müller method[16] and by the Rosenmund method,[18] the latter being somewhat more reliable and providing yields of 75% from the acid. For the synthesis of



XXIII XXIV

the 2 - [γ - (4′ - methoxyphenyl) - propyl] - 3,4,5-trimethoxybenzaldehyde (XXXIV) two routes, involving the two possible chalcone intermediates, were investigated. Thus, *p*-methoxybenzaldehyde was condensed with 3,4,5-trimethoxyacetophenone to give the chalcone XXV and 3,4,5-trimethoxybenzaldehyde was condensed with *p*-methoxyacetophenone to give the chalcone XXVII, both reactions proceeding in almost quantitative yield. The latter chalcone (XXVII) proved preferable, for it made use of somewhat more readily accessible starting materials and also underwent reduction to the diarylpropane more smoothly, providing XXIX in 85% yield. Taking advantage of the fact that polymethoxylated benzenes are readily formylated,[19] the aldehyde XXXIV was prepared in 65–70% yield by the action of N-methylformanilide and phosphorus oxychloride on IX.[20] Formylation of the monomethoxylated ring appeared to take place only to a very small extent.

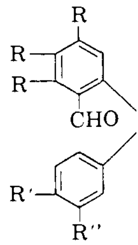


XXV, R = CH₃O, R′ = H
XXVI, R = R′ = CH₃O

XXVII, R = CH₃O, R′ = H
XXVIII, R = R′ = CH₃O

XXIX, R = CH₃O, R′ = H
XXX, R = R′ = CH₃O

In similar fashion 2-[γ-(3′,4′-dimethoxyphenyl)-propyl]-3,4,5-trimethoxybenzaldehyde (XXXV) was synthesized *via* two routes involving the chal-



	R	R′	R″	n
XXXI	H	H	H	2
XXXII	H	CH₃O	H	2
XXXIII	H	H	H	3
XXXIV	CH₃O	CH₃O	H	3
XXXV	CH₃O	CH₃O	CH₃O	3

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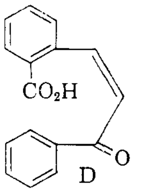
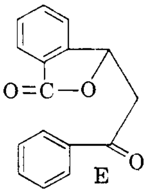
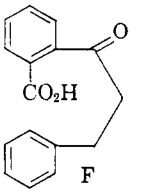
[17] An alternative route to XXIV involved the condensation of 2-carboxybenzaldehyde with acetophenone to give the keto-lactone E resulting from cyclization of the initially-formed chalcone D. Difficulties were encountered in the reduction of E to XXIV, and the method was abandoned in favor of the one described. A second alternative route made use of the condensation of phthalic anhydride with diphenylethylcadmium to give the keto acid F in 50% yield. Although (F) is reducible to XXIV, this method is less satisfactory than the one described above.



D



E

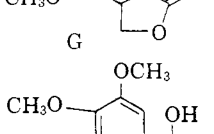


F

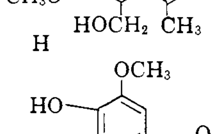
[18] K. W. Rosenmund and F. Zetzsche, *Ber.*, **54**, 425 (1921).

[19] A. H. Sommers, R. J. Michaels and A. W. Weston, THIS JOURNAL, **74** 5546 (1952); *cf.* C. D. Gutsche and E. F. Jason, *ibid.*, **78**, 1184 (1956), for an extension of this reaction to trimethoxybenzene.

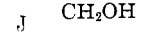
[20] Before the possibility of introducing the aldehyde group at the last step was realized, several other approaches to XXXIV were investigated in which functional groups at the aldehyde position were introduced early in the synthetic sequence: (a) In the hope of preparing 2-hydroxymethyl-3,4,5-trimethoxyacetophenone (H) and employing it in the chalcone route, the action of methylmagnesium iodide and methyllithium on 3,4,5-trimethoxyphthalide (G) was investigated. However, methylmagnesium iodide yielded mainly recovered starting material, methyllithium in excess gave compound J, and methyllithium in equivalent amount gave compound K. (b) In the hope of preparing 2-carboxy-3,4,5-trimethoxyacetophenone and employing it in the chalcone route, the reaction between 3,4,5-trimethoxyphthalic acid and malonic acid was investigated. Only starting material could be isolated, however. (c) A third route involved the conversion of 3,4,5-trimethoxyphenylpropionic acid to the cyano derivative (M) *via* the bromo compound. The attempted conversion of the acid chloride of M to the cyano ketone N by action of *p*-methoxyphenylmagnesium bromide or *p*-methoxyphenyllithium was unsuccessful.



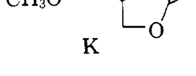
G



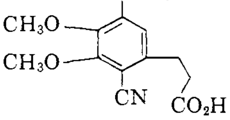
H



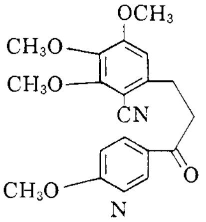
J



K

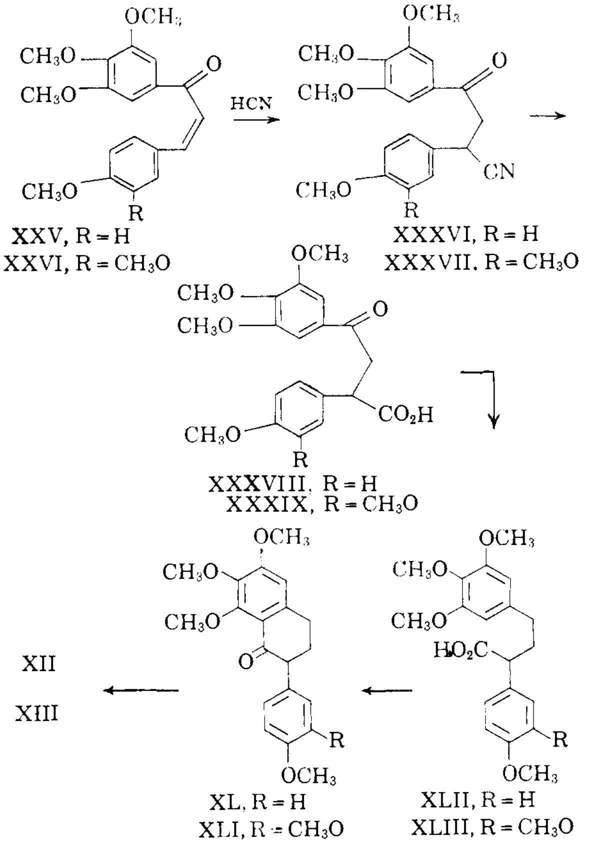


M



N

cones XXVI and XXVIII. Here, also, the latter chalcone (XXVIII) proved to be the more readily reducible to the diarylpropane XXX,[21] the over-all yield of XXX from 3,4,5-trimethoxybenzaldehyde and 3,4-dimethoxyacetophenone being *ca.* 75%. Treatment of XXX with N-methylformanilide and phosphorus oxychloride afforded a mixture containing approximately 60% of the desired monoaldehyde XXXV and 10% of the dialdehyde, the latter being separable by extraction with sodium bisulfite solution.



Conversion of the aldehydes XXXI-XXXV to the diazo compounds I-V involved formation of the hydrazones followed by oxidation with mercuric oxide or silver oxide. On the basis of the nitrogen evolution during the decomposition of the diazo compounds, the over-all yields from the aldehydes are estimated at 55–65%.

Synthesis of Authentic Samples of Indan and Tetralin Compounds.—2-(*p*-Methoxyphenyl)-indan (VII) was synthesized by condensation of *p*-methoxyphenylacetic acid with benzaldehyde to form 1-carboxy-1-(*p*-methoxyphenyl)-2-phenylethylene, reduction and cyclization to 2-(*p*-methoxyphenyl)-indanone, and hydrogenolysis to VII. 2-Benzylindan (XIV) was prepared by cyclization of dibenzylacetic acid with subsequent hydrogenolysis of the resulting benzylindanone. For the synthesis of the tetralin derivatives XII and XIII the chalcones XXV and XXVI proved to be useful starting materials. Addition of hydrogen cyanide to XXV and XXVI gave XXXVI and XXXVII in 94 and 91% yield, hydrolysis converted the cyano ketones to the cyano acids XXXVIII and XXXIX in 64 and 53% yield, and catalytic hydrogenolysis produced the saturated acids XLII and XLIII in quantitative yield.

Cyclization with polyphosphoric acid and then catalytic hydrogenolysis yielded the tetralins XII and XIII in fair yield.[22] In similar fashion 2-phenyltetralin was synthesized from benzalacetophenone.[23]

Acknowledgment.—In addition to the support cited in reference 1 we are indebted to the Petrolite Corporation for aid in the purchase of several items of equipment which greatly facilitated this research.

Experimental[24-25]

Phenylcycloheptatriene.—A solution containing phenyldiazomethane, prepared by mercuric oxide oxidation of 30.0 g. (0.25 mole) of benzalhydrazone, in 500 ml. of benzene was added over a period of 12 hr. to 3.5 l. of refluxing benzene contained in a 5-liter flask. The reaction was allowed to proceed for 72 hr. by which time the original orange color of the solution had changed to a pale yellow and the total nitrogen evolution amounted to 49% of theory. The benzene was removed by distillation through a Claisen head, and the residue was fractionated through a short column to give 5.4 g. (13%) of material with b.p. 77–87° (0.7 mm.). A center cut (b.p. 85–86°) had n^{25}D 1.5993, λ_{max}^{EtOH} (ϵ) 233 mμ (13,500), 300 mμ (9500).[26]

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.20; H, 7.67.

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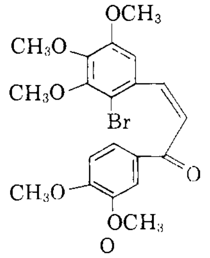
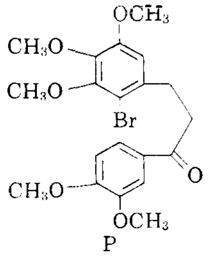
(21) However, an earlier synthetic attempt involving the reduction of the chalcone O resulting from 2-bromo-3,4,5-trimethoxybenzaldehyde and 3,4-dimethoxyacetophenone failed at this point, the only isolable product being the saturated ketone P.

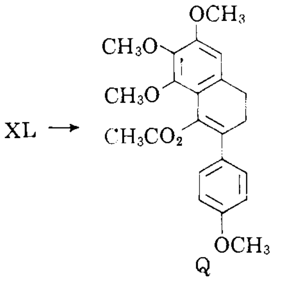


O

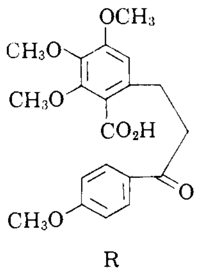


P

(22) One of the attempts to synthesize aldehyde XXIV involved the 2-aryltetralone XL as an intermediate in the formation of the keto acid R. Although the conversion of XL to R could be effected by ozonolysis of the enol acetate Q, the yields were poor and the product resisted further hydrogenolysis to the saturated acid.



Q



R

(23) *Cf.*, for instance, M. S. Newman, This Journal, **60**, 2947 (1938), and H. M. Crawford, *ibid.*, **61**, 608 (1939), for early references to this general method.

(24) All m.p.'s are corrected; all b.p.'s are uncorrected.

(25) The ultraviolet spectra were obtained on a Cary recording spectrophotometer; the infrared spectra were obtained on a Perkin-Elmer model 21 recording spectrophotometer.

(26) A. C. Cope and A. A. D'Addieco, This Journal, **73**, 3419 (1951), have reported a phenylcycloheptatriene with λ_{max} (ϵ) 230 mμ (17,700) and 285 mμ (10,000). W. von E. Doering and L. H. Knox, *ibid.*, **75**, 297 (1953), have reported a phenylcycloheptatriene with λ_{max} (ϵ) 238 mμ (14,500) and 295 mμ (6350).

The maleic anhydride derivative of phenylcycloheptatriene was obtained as colorless needles after several recrystallizations from ethyl acetate–petroleum ether (b.p. 63–67°), m.p. 196–197°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.67; H, 5.28.

Hydrogenation of phenylcycloheptatriene with 5% palladium-on-charcoal as catalyst resulted in the rapid uptake of two mole equivalents of hydrogen and the much slower uptake of an additional 0.5 mole equivalent. The product was identified as phenylcycloheptane through conversion to the 2,4-diacetamino derivative; m.p. 239–241° (reported[27] 240–241°). The same derivative of authentic phenylcycloheptane, prepared from phenylmagnesium bromide and cycloheptanone, then by dehydration and hydrogenation, showed no depression in m.p. when admixed with this sample.

Preparation of 2-(Arylalkyl)-benzaldehydes (XXXII–XXXV)

2-[β-(4′-Methoxyphenyl)-ethyl]-benzaldehyde (XXXII): (A) **4-Methoxybenzal Phthalide** (XXI).—Following a procedure patterned after that of Weiss,[28] 50 g. (0.30 mole) of *p*-methoxyphenylacetic acid (m.p. 85–88°) was condensed with 37.0 g. (0.25 mole) of phthalic anhydride in the presence of 1.5 g. of freshly fused sodium acetate. The crude product was obtained in 82% yield as yellow needles, m.p. 145–147°, which produced colorless needles upon recrystallization from 95% ethanol; m.p. 148–149°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 75.99; H, 4.79.

(B) **4-Methoxybenzyl Phthalide**:—Reduction of 4-methoxybenzal phthalide with 5% palladium-on-charcoal catalyst and hydrogen at 2.5 atmospheres was complete in 14 hr. and gave a quantitative yield of material with m.p. 84–88°. Recrystallization from 95% ethanol gave colorless blades; m.p. 88–89°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.56; H, 5.58.

(C) **2-[β-(4′-Methoxyphenyl)-ethyl]-benzoic Acid** (XXII).—A mixture of 56.0 g. (0.22 mole) of 4-methoxybenzyl phthalide (m.p. 84–88°), 150 ml. of 95% ethanol and 32.5 g. (0.58 mole) of potassium hydroxide was heated to 180° (ethanol evaporated) and maintained at this temperature until the mixture had completely solidified. The mixture was cooled to 100°, dissolved in 150 ml. of water, cooled to room temperature, and then extracted with two portions of ether. The aqueous phase was treated with two teaspoonsful of Raney nickel catalyst and hydrogenated at 2.5 atmospheres of pressure for 20–30 hr. The product consisted of 46.0 g. (82%) of a pale tan solid, m.p. 110–116°, from which an analytical sample was obtained by two recrystallizations from aqueous ethanol; m.p. 119–120°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.64; H, 6.37.

(D) **2-[β-(4′-Methoxyphenyl)-ethyl]-benzanilide**.—A 65.7-g. sample (0.26 mole) of the acid XXII prepared as described above, was converted to the acid chloride with thionyl chloride and then to the anilide by treatment at 10–15° with aniline. The product consisted of 78.8 g. (92.5%) of a nearly colorless material, m.p. 148–150°, from which an analytical sample was obtained as colorless, feathery needles by recrystallization from ethanol; m.p. 152–153°.

Anal. Calcd. for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39. Found: C, 79.63; H, 6.39.

(E) **2-[β-(4′-Methoxyphenyl)-ethyl]-benzaldehyde** (XXXII).—Following the general procedure of Natelson and Gottfried[29] a 78.7-g. sample of the anilide (crude material prepared as described above) was converted to the chloroimide and reduced with stannous chloride and hydrogen chloride to give 23.4 g. (41%) of the aldehyde as an oil, b.p. 150° (0.2 mm.), $n^{25}D$ 1.5820, $\bar{\nu}_{max}^{liq}$ 1695 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.92; H, 6.72.

The 2,4-dinitrophenylhydrazone of XXXII was obtained, after several recrystallizations from ethanol, as pale orange needles, m.p. 172–174°.

Anal. Calcd. for $C_{22}H_{20}N_4O_5$: C, 62.85; H, 4.80. Found: C, 63.14; H, 4.65.

2-[β-(4′-Methoxyphenyl)-ethyl]-benzalazine was prepared from the aldehyde XXXII and hydrazine and obtained, after several recrystallizations from methanol, as pale yellow needles, m.p. 139–140°

Anal. Calcd. for $C_{32}H_{32}N_2O_2$: C, 80.64; H, 6.77. Found: C, 80.51; H, 6.65.

2-(γ-Phenylpropyl)-benzaldehyde (XXXIII). (A) **Phenylacetalphthalide** (**Enol Lactone** XXIII).—2-Carboxyacetophenone was prepared[30] from phthalic anhydride and malonic acid in 42% yield. Condensation with benzaldehyde in a solution of ethanol and 10% aqueous sodium hydroxide at room temperature yielded the chalcone which was not isolated (*cf.* below) but reduced directly with Raney nickel catalyst and hydrogen at 2.5 atmospheres of pressure. After 10–15 hr. the hydrogen uptake (86% of theory for 1 mole-equivalent) ceased, and the product was worked up to give 73% of material presumed to be the dihydro-chalcone. Distillation of this material yielded the enol lactone (65% yield from the chalcone), obtained as thick prisms upon recrystallization from ethanol; m.p. 98–99°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.22; H, 5.08.

In other experiments benzal-2-carboxyacetophenone was isolated, purified by recrystallization from ethanol, and obtained as colorless needles, m.p. 152.5–153.5°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.32; H, 4.66.

(A) **2,4-dinitrophenylhydrazone derivative of benzal-2-carboxyacetophenone** was obtained, after three recrystallizations from ethyl acetate, as pale red needles, m.p. 245–246°.

Anal. Calcd. for $C_{22}H_{16}N_4O_6$: C, 61.11; H, 3.73. Found: C, 60.82; H, 3.43.

(B) **2-(γ-Phenylpropyl)-benzoic Acid** (XXIV).—Following the general procedure of Cope and Fenton[31] a mixture of 42 g. (0.18 mole) of the enol lactone XXIII, 12 g. of red phosphorus and 250 ml. of 57% hydriodic acid was refluxed for 6 hr. An additional 12 g. of red phosphorus was added and refluxing was continued for 14 hr. The product consisted of 37.0 g. (90%) of crude acid, m.p. 79–87°, which, after one crystallization from 70% ethanol, gave 32.5 g. (75%) of colorless material with m.p. 87–90°. An analytical sample was obtained by several further recrystallizations from 70% aqueous ethanol in the form of colorless needles, m.p. 93–94°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.76; H, 6.74.

(C) **2-(γ-Phenylpropyl)-benzanilide**.—A 38-g. sample of the acid XXIV was converted to the acid chloride with phosphorus pentachloride and then to the anilide. The crude product, m.p. 97–100°, obtained in 96% yield, was purified for analysis by recrystallization from aqueous ethanol and obtained as colorless needles, m.p. 101–102°.

Anal. Calcd. for $C_{22}H_{21}NO$: C, 83.77; H, 6.71. Found: C, 83.59; H, 6.66.

(D) **2-(γ-Phenylpropyl)-benzaldehyde** (XXXIII).—Following previously described procedures[29] the anilide, described above, was converted to the chloroimide and reduced with stannous chloride and hydrogen chloride to give the aldehyde XXXIII in 50% yield as a greenish oil. A sample distilled for analysis had b.p. 142–145° (0.5 mm.), $n^{25}D$ 1.5770, $\bar{\nu}_{max}^{liq}$ 1710 cm.$^{-1}$; λ_{max}^{EtOH} (ϵ) 217 mμ (17,500), 253 mμ (8750), 295 mμ (1420).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.42; H, 6.98.

The 2,4-dinitrophenylhydrazone of XXXIII was obtained as red needles after several recrystallizations from ethyl acetate; m.p. 206–207°.

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(27) A. C. Cope and A. A. D'Addieco, THIS JOURNAL, **73**, 3419 (1951).

(28) R. Weiss, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 61.

(29) S. Natelson and S. P. Gottfried, THIS JOURNAL, **58**, 1432 (1936).

(30) H. L. Yale, *ibid.*, **69**, 1547 (1947).

(31) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1668 (1951).

Anal. Calcd. for $C_{22}H_{10}N_4O_4$: C, 65.33; H, 4.99. Found: C, 65.34; H, 4.74.

The azine of XXXIII was obtained as blunt, yellow needles after recrystallization from methanol; m.p. 66–67°.

Anal. Calcd. for $C_{32}H_{32}N_2$: C, 86.44; H, 7.26. Found: C, 86.11; H, 7.33.

Conversion of the acid to the aldehyde *via* the Rosenmund reduction followed the general procedure used by Tarbell, *et al.*[32] A 36.0-g. sample of the acid was converted to the acid chloride with phosphorus pentachloride, dissolved in 250 ml. of xylene, and hydrogenated in the presence of 10 g. of palladium–barium sulfate catalyst and 1 ml. of sulfur–quinoline poison to give 23.5 g. (75%) of aldehyde as a yellow oil, b.p. 143–147° (0.5 mm.), n^{25}D 1.5780.

2-[γ-(4′-Methoxyphenyl)-propyl]-3,4,5-trimethoxybenzaldehyde (XXXIV). (A) **4′-Methoxybenzal-3,4,5-trimethoxyacetophenone (XXV).**—3,4,5-Trimethoxyacetophenone was prepared by a procedure patterned after one described by Wilds and Beck.[33] From a reaction employing 173 g. (0.75 mole) of 3,4,5-trimethoxybenzoyl chloride, 360 g. (2.25 moles) of diethyl malonate, 34.5 g. (1.5 g.-atoms) of sodium and 2 liters of ether there was obtained 223 g. (84%) of diethyl 3,4,5-trimethoxybenzoylmalonate, m.p. 83–87°. Recrystallization from ethyl acetate–petroleum ether (b.p. 63–69°) gave glistening white needle m.p. 91–92°.

Anal. Calcd. for $C_{17}H_{22}O_8$: C, 57.72; H, 6.62. Found: C, 57.47; H, 6.16.

Conversion of the diethyl 3,4,5-trimethoxybenzoylmalonate to 3,4,5-trimethoxyacetophenone with 25% sulfuric acid proceeded in 58% yield and gave the ketone as a colorless solid with m.p. 75–78° (reported[34] 78°). A mixture of 38.0 g. (0.18 mole) of the ketone, 24.5 g. (0.19 mole) of anisaldehyde, 150 ml. of 50% aqueous ethanol and 20 ml. of trimethylbenzylammonium hydroxide solution was stirred at 40° for 12 hr. and then cooled to 5° for several hr. Filtration gave 56.5 g. (95%) of the chalcone XXV as a yellow powder, m.p. 98–100°, which was purified by recrystallization from ethanol and obtained as light yellow prisms, m.p. 100–101°.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.04; H, 6.04.

(B) **3,4,5-Trimethoxybenzal-4′-methoxyacetophenone (XXVII).**—A mixture of 81 g. (0.41 mole) of 3,4,5-trimethoxybenzaldehyde,[32] 62 g. (0.41 mole) of 4-methoxyacetophenone, 150 ml. of ethanol and 150 ml. of 10% aqueous sodium hydroxide was stirred at room temperature for 4 hr. and then cooled to 5°. Filtration gave 125 g. (94%) of the chalcone XXVII as a yellow powder, m.p. 130–132°, which was recrystallized from ethanol and obtained as yellow needles, m.p. 131–132°.

Anal. Calcd. for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.04; H, 6.04.

(C) **3,4,5-Trimethoxy-(γ-(4′-methoxyphenyl)-propyl]-benzene (XXIX).**—A 32.8 g. sample of the chalcone XXV was suspended in 200 ml. of ethyl acetate, treated with 15 g. of 5% palladium-on-charcoal catalyst and 4 ml. of 70% perchloric acid, and subjected to 2.5 atmospheres of hydrogen pressure for 30 hr. The product was distilled to give 25.5 g. (81%) of a colorless liquid, b.p. 185–205° (0.5 mm.), which slowly solidified; m.p. 45–53°. Recrystallization from petroleum ether (b.p. 63–69°) gave colorless, blunt needles, m.p. 57.5–58.5°.

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 71.86; H, 7.52.

If the perchloric acid was omitted in the hydrogenation, the uptake ceased after one mole-equivalent had been absorbed and a quantitative yield of a material with m.p. 93–94° after recrystallization from ethyl acetate–petroleum ether (b.p. 63–69°) was obtained. This material is thought to be **1-keto-1-(4′-methoxyphenyl)-3-(3′,4′,5′-trimethoxyphenyl)-propane.**

Anal. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.40; H, 6.55.

A **2,4-dinitrophenylhydrazone** of **1-keto-1-(4′-methoxyphenyl)-3-(3′,4′,5′-trimethoxyphenyl)-propane** was obtained, after several recrystallizations from ethyl acetate, as brilliant red, microscopic crystals, m.p. 212–213°.

Anal. Calcd. for $C_{25}H_{26}N_4O_8$: C, 58.82; H, 5.13. Found: C, 58.72; H, 4.81.

A second route to XXIX involved the reduction of the chalcone XXVII. A 60-g. sample of XXVII suspended in 300 ml. of glacial acetic acid was treated with 7 g. of 5% palladium-on-charcoal catalyst and subjected to 2.5 atmospheres of hydrogen pressure for 20 hr. The product consisted of 54.5 g. (95%) of a white powder, m.p. 55–57°, identical with the material reported above from the reduction of the chalcone XXV.

(D) **2-[γ-(4′-Methoxyphenyl)-propyl]-3,4,5-trimethoxybenzaldehyde (XXXIV).**—Following previously described procedures,[19] a mixture of 41.2 g. (0.27 mole) of phosphorus oxychloride and 36.5 g. (0.27 mole) of N-methylformanilide was prepared and allowed to stand for *ca.* 1 hr. To this stirred mixture was added 55.0 g. (0.17 mole) of 3,4,5-trimethoxy-[γ-(4′-methoxyphenyl)-propyl]-benzene (XXIX) (m.p. 55–57°). The reaction mixture was stirred at room temperature for 14 hr. and then poured into water and ether extracted. The ether extract was shaken for several hours with 200 ml. of saturated sodium bisulfite solution and separated and dried. Evaporation of the ether and distillation of the residue gave 43.5 g. of material with b.p. 210–225° (1 mm.) which was redistilled to give a slightly yellow, viscous oil, b.p. 202–210° (0.5 mm.), n^{25}D 1.5695, $\bar{\nu}_{\max}^{\text{liq}}$ 1680 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.63; H, 7.21.

The 2,4-dinitrophenylhydrazone of XXXIV was obtained, after several recrystallizations from ethanol–ethyl acetate, as glistening, magenta needles, m.p. 140–141°.

Anal. Calcd. for $C_{26}H_{28}N_4O_8$: C, 59.53; H, 5.38. Found: C, 59.23; H, 5.28.

The semicarbazone of XXXIV was obtained, after several recrystallizations from ethyl acetate–petroleum ether (b.p. 63–69°), as colorless, feathery needles, m.p. 154–155°.

Anal. Calcd. for $C_{21}H_{27}N_3O_5$: C, 62.82; H, 6.78. Found: C, 62.53; H, 6.61.

Decomposition of the bisulfite layer (*cf.* above) with 20% sodium hydroxide solution followed by ether extraction yielded a small amount of an oil which could be converted to a 2,4-dinitrophenylhydrazone. This is presumed to be the **2,4-dinitrophenylhydrazone of the dialdehyde XXXIV** with a second formyl group (probably in the monomethoxylated ring) and was obtained as a very dark red product after several recrystallizations from ethyl acetate; m.p. 210–213°.

Anal. Calcd. for $C_{33}H_{32}N_8O_{12}$: C, 54.09; H, 4.40. Found: C, 53.60; H, 4.32.

2-[γ-(4′-Methoxyphenyl)-propyl]-3,4,5-trimethoxybenzalazine was obtained from XXXIV and hydrazine as bright yellow blades after several recrystallizations from 95% ethanol; m.p. 132.5–133.5°.

Anal. Calcd. for $C_{40}H_{48}N_2O_8$: C, 70.15; H, 7.07. Found: C, 69.88; H, 7.00.

2-[γ-(3′,4′-Dimethoxyphenyl)-propyl]-3,4,5-trimethoxybenzaldehyde (XXXV). (A) **3′,4′-Dimethoxybenzal-3,4,5-trimethoxyacetophenone (XXVI).**—A mixture of 10.5 g. (0.05 mole) of 3,4,5-trimethoxyacetophenone, prepared as described above, 8.5 g. (0.05 mole) of veratraldehyde, 50 ml. of 50% aqueous ethanol and 5 ml. of trimethylbenzylammonium hydroxide was stirred for 9 hr. at 40°. The product consisted of 18.5 g. (93%) of the chalcone XXVI, m.p. 126–130°, which yielded yellow needles after two recrystallizations from 95% ethanol; m.p. 134–135°.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19. Found: C, 66.60; H, 5.83.

(B) **3,4,5-Trimethoxybenzal-3′,4′-dimethoxyacetophenone (XXVIII).**—A mixture of 67.6 g. (0.345 mole) of 3,4,5-trimethoxybenzaldehyde,[32] 62.0 g. (0.345 mole) of 3,4-dimethoxyacetophenone,[35] 300 ml. of 50% aqueous ethanol and 7 g. of sodium hydroxide was stirred for 7 hr. at room temperature. The product consisted of 113 g. (94%) of the chalcone XXVIII obtained as yellow needles after recrystallization from 95% ethanol; m.p. 134–135°.

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[32] H. T. Huang, D. S. Tarbell and H. R. V. Arnstein, THIS JOURNAL, **70**, 4181 (1948).

[33] A. L. Wilds and L. W. Beck, *ibid.*, **66**, 1688 (1944).

[34] F. Mauthner, *J. prakt. Chem.*, [2] **82**, 271 (1910); **115**, 137 (1927).

[35] J. B. Koepfli and W. H. Perkin, *J. Chem. Soc.*, 2989 (1928).

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.02; H, 6.19. Found: C, 66.71; H, 6.08.

(C) **3,4,5-Trimethoxy-[γ-(3′,4′-dimethoxyphenyl)-propyl]-benzene (XXX).**—Attempts to hydrogenate the chalcone XXVI were unsuccessful. However, when chalcone XXVIII was dissolved in ethyl acetate, treated with 5% palladium-on-charcoal catalyst and 4 ml. of 70% perchloric acid, and hydrogenated for 24 hr. at 2.5 atmospheres pressure, an 80% yield of XXX was obtained as a clear, viscous oil, b.p. 200–205° (0.5 mm.), $n^{25}\text{D}$ 1.5671. Crystallization was induced by dissolving in ethyl acetate–petroleum ether (b.p. 63–69°) and cooling to −70°. Further recrystallizations from the same solvent mixture gave colorless rosettes; m.p. 54–55°.

Anal. Calcd. for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 68.99; H, 7.38.

A pentabromo derivative of XXX was obtained, after two recrystallizations from 95% ethanol, as colorless needles, m.p. 129–130°.

Anal. Calcd. for $C_{20}H_{21}Br_5O_5$: C, 32.39; H, 2.80. Found: C, 32.05; H, 2.76.

If the perchloric acid was omitted in the hydrogenation, the uptake ceased after one mole-equivalent had been absorbed, and a quantitative yield of a material in the form of blunt needles with m.p. 101–102° after recrystallization from 95% ethanol was obtained. This compound is thought to be **1-keto-1-(3′,4′-dimethoxyphenyl)-3-(3′,4′,5′-trimethoxyphenyl)-propane.**

Anal. Calcd. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.58; H, 6.59.

(D) **2-[γ-(3′,4′-Dimethoxyphenyl)-propyl]-3,4,5-trimethoxybenzaldehyde (XXXV).**—Formylation was effected as described above for the conversion of XXIX to XXXIV. From 64.6 g. of 3,4,5-trimethoxy-[γ-(3′,4′-dimethoxyphenyl)-propyl]-benzene (XXX) there was obtained 6.1 g. (8%) of bisulfite-soluble material and 51.2 g. of bisulfite-insoluble material. Redistillation of the latter through a 4-inch Vigreux column gave 42.1 g. (61%) of a pale yellow oil from which a center cut had b.p. 212° (0.5 mm.), $n^{25}\text{D}$ 1.5780, $\bar{\nu}^{\text{liq}}_{\max}$ 1680 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.72; H, 6.71.

The semicarbazone of XXXV was obtained, after recrystallization from 95% ethanol, as colorless, feathery needles, m.p. 169–170°.

Anal. Calcd. for $C_{22}H_{29}N_3O_6$: C, 61.24; H, 6.77. Found: C, 61.26; H, 6.45.

2-[γ-(3′,4′-Dimethoxyphenyl)-propyl]-3,4,5-trimethoxybenzalazine was obtained, after recrystallization from 95% ethanol, as pale yellow, blunt needles, m.p. 138–139°.

Anal. Calcd. for $C_{42}H_{52}N_2O_{10}$: C, 67.72; H, 7.04. Found: C, 67.62; H, 6.91.

Decomposition of the bisulfite-soluble portion (*cf.* above) yielded an oil from which a 2,4-dinitrophenylhydrazone could be obtained as a dull red powder, m.p. 266–268°. Presumably this is the 2,4-dinitrophenylhydrazone of the dialdehyde (XXXV with a second formyl group, probably in the di-methoxylated ring).

Anal. Calcd. for $C_{34}H_{34}N_8O_{13}$: C, 53.54; H, 4.46. Found: C, 52.98; H, 4.33.

Preparation and Reaction of 2-(Arylalkyl)-phenyl diazomethanes (II–V)

2-[β-(4′-Methoxyphenyl)-ethyl]-phenyldiazomethane (II). (A) **Preparation.**—To a stirred mixture of 4 ml. (0.25 mole) of anhydrous hydrazine and 50 ml. of anhydrous ether a solution of 10.0 g. (0.041 mole) of 2-[β-(4′-methoxyphenyl)-ethyl]-benzaldehyde (XXXII) in 50 ml. of anhydrous ether was added slowly, the temperature being maintained at 0–5°. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stand overnight. The ether then was evaporated under reduced pressure leaving 10.5 g. (100%) of a viscous oil, $n^{25}\text{D}$ 1.5966, which eventually solidified; m.p. 17–19°. Without further purification this material was dissolved in 150 ml. of petroleum ether (b.p. 63–69°) and treated with 13.0 g. (0.06 mole) of red mercuric oxide. The mixture was stirred at 28° for 3.5 hr., by which time it had become pale red, and was then filtered to remove the solid materials. A small sample was evaporated leaving a thick red oil, $\bar{\nu}^{\text{liq}}_{\max}$ 2070 cm.$^{-1}$. The remainder of the material was used without further purification.

(B) **Photolysis.**—The product described above was diluted to 2 liters with petroleum ether (b.p. 63–69°) and irradiated at reflux temperature for 64 hr. by means of a General Electric RS sunlamp. By this time the nitrogen evolution had ceased, and the solution had become pale yellow. Removal of the solvent by evaporation and distillation of the residue through a 4-inch Vigreux column gave 4.12 g. (46%) of volatile material boiling over the range 125–165° (0.5 mm.). A lower boiling fraction amounting to 1.66 g. had the physical properties, b.p. 132–135°(0.5 mm.), $n^{25}\text{D}$ 1.5928; $\lambda^{\text{EtOH}}_{\max}$ (ε) 218 mμ (11,800), 234 mμ (4370), 255 mμ (2380), 275 mμ (2260), 285 mμ (2260), 300 mμ (1240). The absorption bands at 234 and 300 are taken as indicative of the presence of the tricyclic cycloheptatriene VII. Treatment of the crude product with 2,4-dinitrophenylhydrazine yielded the 2,4-dinitrophenylhydrazone of the aldehyde XXXII in 10% yield from II. Chromatography on a 1.2 × 25 cm. column of alumina of a 1.50-g. sample of the fraction with b.p. 132–135° (0.5 mm.) gave 0.95 g. of 2-(4′-methoxyphenyl)-indan (IX) (elution with petroleum ether of b.p. 63–69°) and 0.37 g. of a mixture of aldehyde XXXIII and what is presumed to be 2-[β-(4′-methoxyphenylethyl]-benzonitrile (elution with benzene–petroleum ether and then benzene–chloroform), the latter identified only by the presence of an absorption band in the infrared at 2230 cm.$^{-1}$. Re-chromatography of the first fraction yielded a pure sample of the indan which was identical with an authentic sample, prepared as described under "miscellaneous experiments." The indan was converted to a diacetyl derivative, m.p. 106–107°, which showed no depression in m.p. when admixed with an authentic sample.

2-(γ-Phenylpropyl)-phenyldiazomethane (III). (A) **Preparation.**—To a vigorously stirred suspension of 3.2 g. (0.1 mole) of anhydrous hydrazine in 50 ml. of absolute ether a solution of 6.0 g. (0.026 mole) of 2-(γ-phenylpropyl)-benzaldehyde (XXXIII) in 50 ml. of absolute ether was added over a period of 1 hr., the temperature being maintained at 0–5°. The reaction mixture was stirred overnight at 5° and then allowed to warm to room temperature and stirred an additional 4–5 hr. The ethereal solution was washed twice with 10-ml. portions of water, dried over sodium sulfate, diluted to 100 ml. with ether,[36] and placed in a 300-ml. flask fitted with a stirrer. The air in the flask was replaced with nitrogen, the flask was cooled in an ice-bath, and the stirred mixture was treated with 10 g. of anhydrous sodium sulfate and 10 g. (0.041 mole) of silver oxide. After stirring for 10–20 min. at 0–5°, the mixture was filtered, and the volatile materials were removed at 0° under reduced pressure to leave 6.0 g. (99%) of a deep red oil, $\bar{\nu}^{\text{liq}}_{\max}$ 2060 cm.$^{-1}$. An infrared absorption band at 1695 cm.$^{-1}$ indicates the presence of aldehyde in the diazo preparation; under optimum conditions this was very weak or missing, but if the oxidation was carried out in the presence of air the aldehyde band was strong.

(B) **Preparative Photolysis Experiment.**—The diazo compound III from 23.0 g. of aldehyde XXXIII was dissolved in 6 l. of petroleum ether (b.p. 63–69°; purified by washing with concentrated sulfuric acid and water, drying over phosphorus pentoxide, and distilling from sodium) and placed in a 12-l. flask fitted with an efficient reflux condenser. The system was evacuated and filled with oxygen-free nitrogen, and the solution was refluxed and irradiated with two General Electric RS lamps for 54 hr. during which time 2.5 l. (65%) of nitrogen was evolved. The solvent was removed at atmospheric pressure, and the residue was distilled through a Claisen flask to give 9.5 g. of a pale yellow oil, b.p. 100–150° (0.5 mm.). This material was distilled through a Piros–Glover spinning band column, and 5 fractions were collected and identified as described below.

Fraction a contained 0.94 g. of material with b.p. 84–110° (0.4 mm.). It was dissolved in petroleum ether (b.p. 63–69°), adsorbed on a 1.2 × 25 cm. column of alumina (Woelm-Eschwege neutral grade), and the column eluted with 160 ml. of petroleum ether (b.p. 63–69°) collected in 8 fractions. All of the fractions had an absorption band at 235 mμ (ε *ca.*

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[36] In some cases 2 ml. of saturated alcoholic potassium hydroxide (*cf.* C. D. Nenitzescu and E. Solominica, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 496) was added at this point, but this was found not to be essential for a rapid oxidation.

1000) with fractions 3 and 4 showing it most strongly. Attempts to obtain a maleic anhydride adduct of the cycloheptatriene compound X were unsuccessful, however. When fraction **a** was treated with acetyl chloride and aluminum chloride a compound was obtained which yielded a 2,4-dinitrophenylhydrazone of m.p. 244–246°. This compound proved to be identical with the 2,4-dinitrophenylhydrazone of the diacetyl derivative of 2-(γ-phenylpropyl)-toluene, prepared as described under "miscellaneous experiments."

Fraction **b** contained 1.58 g. of material with b.p. 110–116° (0.4 mm.). The infrared spectrum of this fraction contained all of the bands present in 2-benzylindan (XIV), and acetylation yielded a compound with m.p. 86–87° identical with the diacetyl derivative of authentic 2-benzylindan, prepared as described under "miscellaneous experiments."

Fraction **c** contained 1.50 g. of material with b.p. 116–126° (0.4 mm.). It was subjected to chromatography as described for fraction **a**, and an oil was obtained which had an infrared spectrum containing all of the bands present in 2-phenyltetralin (XI). Acetylation of this oil yielded a compound with m.p. 136–137° identical with the diacetyl derivative of authentic 2-phenyltetralin, prepared as described under "miscellaneous experiments." The presence of 2-phenyltetralin also was shown by a dehydrogenation of fraction **c** (5% palladium-on-charcoal at 300–330°) to 2-phenylnaphthalene, m.p. 96–98°.

Fraction d contained 0.50 g. of material with b.p. 126–130° (0.4 mm.) and had infrared absorption bands at 2230 (nitrile) and 1695 cm.$^{-1}$ (aldehyde). Chromatography on alumina and elution with petroleum ether (b.p. 63–69°) yielded the nitrile XV as an oil identical in refractive index, infrared spectrum and ultraviolet spectrum with an authentic sample of XV prepared as described under "miscellaneous experiments." Further identification was obtained by hydrolysis to the corresponding acid. A 0.38-g. sample of the nitrile was added to a mixture of 20 ml. of ethanol, 0.2 ml. of 30% hydrogen peroxide and 0.2 ml. of 20% aqueous sodium hydroxide.[37] The reaction mixture was held at 45–50° for 3.5 hr. and then at room temperature overnight. Working up in the usual fashion yielded the amide which was treated with 1.5 ml. of sulfuric acid and 10 ml. of water containing a few drops of acetic acid.[38] The mixture was warmed on the steam-bath for 0.5 hr., cooled to room temperature and treated with a solution of 3.0 g. of sodium nitrite in 5 ml. of water followed by 2 ml. of concentrated sulfuric acid and another 4.0 g. of sodium nitrite in 10 ml. of water, and stirred overnight. The product consisted of 0.21 g. (52%) of 2-(γ-phenylpropyl)-benzoic acid (XXIV) identical with material prepared as described above, m.p. 92–93°.

Fraction e contained 4.20 g. of material with b.p. 130–133° (0.5 mm). It had an infrared and ultraviolet spectrum characteristic for a mixture of aldehyde XXXIII and nitrile XV and yielded a 2,4-dinitrophenylhydrazone which showed no depression in m.p. when admixed with the derivative from authentic XXXIII. From the residue of the distillation of the crude product, 2-(γ-phenylpropyl)-benzalazine was isolated by recrystallization from methanol, m.p. 66–67°. On the basis of weights of distillation fractions and by a comparison of ultraviolet extinction coefficients for various fractions with those of pure components the following estimates for yields are obtained: tricyclic cycloheptatriene X, less than 1%; 2-(γ-phenylpropyl)-toluene, very small amount; 2-benzylindan (XIV) and 2-phenyltetralin (XI) combined, 15%; 2-(γ-phenylpropyl)-benzonitrile (XV), 5–20% depending upon experiment, 2-(γ-phenylpropyl)-benzaldehyde (XXXIII), 0–20% depending upon experiment; azine of XXXIII, *ca.* 25%.

(C) Comparative Decomposition Experiments.—A preparation of 2-(γ-phenylpropyl)-phenyldiazomethane was divided into three equal parts. One aliquot was treated as above by refluxing and irradiating in petroleum ether (b.p. 63–69°). Another aliquot was dissolved in petroleum ether (b.p. 175–183°) and refluxed without irradiation for 18 hr. The third aliquot was dissolved in petroleum ether (b.p. 63–69°) and irradiated for 7 days with a 100 watt ultraviolet lamp placed in a water-cooled quartz well immersed in the solution. The temperature throughout the reaction was 15–18°. The three reaction mixtures were worked up in the same fashion as described. The solvent was evaporated, and the residue was distilled in a small Claisen flask. The distillate then was dissolved in petroleum ether and passed through an alumina column to remove aldehyde and nitrile. The resulting hydrocarbon mixture was assayed by vapor phase chromatography with column temperatures of 225°. Known mixtures of authentic 2-benzylindan and 2-phenyltetralin were also subjected to vapor phase chromatography. The results are shown in Table I. It is very doubtful that the figures in the right-hand column have any precise significance. It does appear definite, however, that there is more tetalin produced in the high temperature experiment than in either of the low temperature experiments. It also appears that the yield of hydrocarbon is improved by operation at lower temperatures (however *cf.* experiments with IV described below).

TABLE I

DECOMPOSITION OF 2-(γ-PHENYLETHYL)-PHENYLDIAZOMETHANE

Reaction conditions	Yield of crude hydrocarbons, %	Shoulder at 235 mμ	Ratio of Indan/tetralin peak heights	Calcd. ratio indan/tetralin
Petr. eth. (b.p. 63–69°) at refl. with irrad.	14	Yes	0.87	6:1
Petr. eth. (b.p. 175–183°) at refl. without irrad.	14	No	.70	2:1
Petr. eth. (b.p. 63–69°) at 15–18° with irrad.	25	Yes	.90	9:1
Indan–tetralin (1:3)			.25	
Indan–tetralin (1:1)			.60	
Indan–tetralin (3:1)			.78	

2-[γ-(4'-Methoxyphenyl)-propyl]-3,4,5-trimethoxyphenyldiazomethane (IV). (A) **Preparation.**—A solution of 15.0 g. (0.044 mole) of 2-[γ-(4'-methoxyphenyl)-propyl]-3,4,5-trimethoxybenzaldehyde (XXXIV) in 50 ml. of anhydrous ether was added, over a period of 30 min., to a mixture of 15 ml. of hydrazine (0.50 mole) in 50 ml. of ether at 5–7°. The mixture became turbid as the aldehyde was added but cleared upon stirring overnight at 5°. The aqueous hydrazine layer was separated, and the ethereal solution was washed with two 20-ml. portions of water and dried over anhydrous sodium sulfate. An infrared spectrum showed no carbonyl absorption. The ethereal solution of hydrazone was treated with 10 g. of anhydrous sodium sulfate and 15 g. (0.069 mole) of yellow mercuric oxide and stirred at room temperature for 4 hr. The pale red solution was filtered and used without purification; $\tilde{\nu}^{\text{ether}}_{\text{max}}$ 2060 cm.$^{-1}$.

(B) **Photolysis.**—The diazo compound from 15.0 g. of aldehyde XXXIV was diluted to 4.0 liters with petroleum ether (b.p. 175–183°) and irradiated at reflux temperature for a period of 24 hr. by means of a General Electric RS sunlamp. The solvent was removed by distillation through a short column, and the residue was dissolved in a small quantity of hot 95% ethanol and allowed to crystallize overnight. Filtration yielded 2.2 g. (15%) of the azine, m.p. 132–133°, and evaporation of the filtrate left 11.5 g. of an oil. A 1.75-g. sample of this was chromatographed on a column of alumina 1.2 × 25 cm. The first eluate (petroleum ether of b.p. 63–69°-benzene), consisted of 0.14 g. of the diarylpropane XXIX, m.p. 53–55°. The second eluate consisted of 0.54 g. (25%) of the tetralin XII, m.p. 80–81°, identical with an authentic sample prepared as described under "miscellaneous experiments" (eluted with petroleum ether of b.p. 63–69°-benzene). The third eluate consisted of 0.45 g. (20%) of a mixture of aldehyde XXXIV and nitrile XVI as indicated by the infrared absorption bands at 1680 and 2240 cm.$^{-1}$ (eluted with benzene and benzene-chloroform). The fourth eluate (chloroform-benzene) contained 0.13 g. (5%) of azine. The last eluate (methanol) consisted of 0.12 g. of material which had an infrared spectrum resembling that of the material obtained from ultraviolet irradiation of the pure aldehyde XXXIV. From a comparable experiment carried out for 18 hr. in refluxing petroleum ether (b.p. 63–69°) the same products were obtained, but the yield of the tetralin XII was only 8%.

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[37] C. R. Noller, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 586.

[38] F. C. Whitmore and D. P. Langlois, THIS JOURNAL, **54**, 3438 (1932).

2-[γ-(3′,4′-Dimethoxyphenyl)-propyl]-3,4,5-trimethoxyphenyldiazomethane (V). (A) Preparation.—A solution of 5.52 g. (0.0148 mole) of 2-[γ-(3′,4′-dimethoxyphenyl)-propyl]-3,4,5-trimethoxybenzaldehyde (XXXV) in 75 ml. of anhydrous ether was added, in one portion, to a suspension of 5 ml. of anhydrous hydrazine in 100 ml. of anhydrous ether at room temperature. The mixture was stirred at room temperature for 19 hr., and the ethereal layer was separated and washed with water and dried. The ether solution was then treated with 3 g. of anhydrous sodium sulfate and 3.0 g. (0.0140 mole) of yellow mercuric oxide, and the reaction mixture was stirred at room temperature for 3.5 hr. Evaporation of the ether under reduced pressure left a red oil which had an absorption band at 2070 cm.$^{-1}$.

(B) Photolysis.—The diazo compound described above was dissolved in 2 liters of petroleum ether (b.p. 63–69°) and irradiated at reflux temperature for a period of 24 hr. by means of a General Electric RS sunlamp. The solvent was removed by distillation through a short column to leave 5.4 g. of a viscous oil, a portion of which was subjected to chromatography on alumina. However, only the azine, m.p. 138–139°, could be isolated by this procedure. Consequently, a 4.0-g. sample of the crude product was dissolved in ethyl acetate, treated with 1.0 g. of 5% palladium-on-charcoal catalyst, and hydrogenated for 24 hr. under 2.5 atmospheres of pressure. The catalyst was removed by filtration, the solvent was evaporated, and the residual oil was dissolved in 100 ml. of ether. The ethereal solution was extracted with dilute hydrochloric acid, washed with water, and dried. Evaporation of the solvent left 1.8 g. of an oil which was chromatographed on a column of alumina 1.2 × 25 cm. Elution with petroleum ether (b.p. 63–69°)-benzene gave 0.24 g. (7%) of the tetralin XIII, m.p. 92–93°, identical with an authentic sample prepared as described under "miscellaneous experiments." The presence of the aldehyde XXXV and the nitrile XVII was indicated by infrared absorption bands at 1680 and 2240 cm.$^{-1}$ in the crude material.

Miscellaneous Experiments

α-Phenacyl Phthalide (Compound E).—A mixture of 4.0 g. (0.026 mole) of 2-carboxybenzaldehyde,[39] 3.1 g. (0.026 mole) of acetophenone, 15 ml. of ethanol, 10 ml. of water and 2.0 g. of sodium hydroxide was stirred for 4 hr. at room temperature. The product consisted of 6.2 g. (93%) of nearly colorless material, m.p. 125–131°. Recrystallization from aqueous ethanol gave colorless needles, m.p. 131–132°, $\bar{\nu}_{max}^{CHCl_3}$ 1760 (γ-lactone carbonyl), 1690 cm.$^{-1}$ (benzoyl carbonyl).

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.28; H, 5.05.

2-(β-Phenylpropionyl)-benzoic Acid (Compound F).—Following well-known procedures[40] the Grignard reagent prepared from 100 g. of 2-phenylethyl bromide was converted to di-(2-phenylethyl)-cadmium. This was then treated at 0° with 32.8 g. of phthalic anhydride, added over a period of 1 hr. The mixture was stirred for 2 hr. on the steam-bath and then was worked up to give 48 g. of a viscous oil which did not crystallize. **A 2,4-dinitrophenylhydrazone** of the keto acid was obtained, after several recrystallizations from 95% ethanol, as pale orange needles, m.p. 196–197°.

Anal. Calcd. for $C_{22}H_{18}N_4O_6$: C, 60.82; H, 4.18. Found: C, 60.63; H, 4.61.

1-Hydroxymethyl-2,3,4-trimethoxy-6-(α-hydroxyisopropyl)-benzene (Compound J).—When 3,4,5-trimethoxyphthalide (compound G)[41] was treated with a 6-fold excess of methyllithium in benzene-ether solution at reflux a 98% crude yield of compound J was obtained. Recrystallization from petroleum ether (b.p. 63–69°) gave colorless feathery needles, m.p. 88.5–89.5°.

Anal. Calcd. for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 61.22; H, 7.75.

1,1-Dimethyl-3,4,5-trimethoxyphthalan was produced by distilling a sample of compound H from potassium acid sulfate and obtained as a colorless, mobile liquid, b.p. 119–120° (1.0 mm.), $n^{25}D$ 1.5208.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.43; H, 7.58.

3,5-Dimethoxy-4-hydroxyphthalide (compound K) was obtained when 3,4,5-trimethoxyphthalide was treated with one equivalent of methylmagnesium bromide in benzene-ether solution at reflux or in tetrahydrofuran solution at reflux. The identification was based on its solubility in 10% sodium hydroxide solution, a positive test with ferric chloride, and the correspondence in m.p. with the reported value.[42]

β-(2-Cyano-3,4,5-trimethoxyphenyl)-propionic Acid (Compound M).—A 9.6-g. sample (0.03 mole) of β-(2-bromo-3,4,5-trimethoxyphenyl)-propionic acid[43] was thoroughly mixed with 3.0 g. (0.033 mole) of cuprous cyanide. One-third of this mixture was placed in a 6-inch test-tube and heated in an oil-bath at 240°. When the temperature of the mixture spontaneously rose to *ca.* 260°, the test-tube was removed from the oil-bath and allowed to cool to *ca.* 220°. The remaining mixture of bromo-acid and cuprous cyanide then was added in portions over a 20-min. period while the temperature was maintained at 240°. After heating an additional 15 min. the mixture was cooled to room temperature and extracted with boiling acetone. The acetone was removed by evaporation, the residue was extracted with 10% sodium hydroxide solution, and the basic extract was washed with ether. Acidification of the basic extract then yielded 4.30 g. (54%) of the cyano acid M as tan needles, m.p. 125–128°, from which an analytical sample was obtained as colorless blades after several recrystallizations from petroleum ether (b.p. 88–98°)-ethyl acetate; m.p. 132–133°.

Anal. Calcd. for $C_{13}H_{15}NO_5$: C, 58.85; H, 5.70. Found: C, 59.26; H, 5.93.

2-Bromo-3,4,5-trimethoxybenzal-3′,4′-dimethoxyacetophenone (Compound O). (A) Preparation of 2-Bromo-3,4,5-trimethoxybenzaldehyde.—A 57.4-g. (0.197 mole) sample of 2-bromo-3,4,5-trimethoxybenzoic acid[44] was treated with thionyl chloride to give 44 g. (72%) of distilled acid chloride, b.p. 162–163° (0.5 mm.), which slowly solidified, m.p. 75–79°. The acid chloride then was subjected to a Rosenmund reduction to yield 40.7 g. (42%) of bisulfite-soluble material, m.p. 63–65°. Several recrystallizations from aqueous ethanol gave colorless needles, m.p. 70.5–71.5°.

Anal. Calcd. for $C_{10}H_{11}BrO_4$: C, 43.66; H, 4.03. Found: C, 44.05; H, 4.22.

The 2,4-dinitrophenylhydrazone of 2-bromo-3,4,5-trimethoxybenzaldehyde was obtained, after several recrystallizations from acetone, as brilliant red prisms, m.p. 239–240.5°.

Anal. Calcd. for $C_{16}H_{15}BrN_4O_7$: C, 42.21; H, 3.32. Found: C, 42.23; H, 3.21.

(B) Synthesis of the Chalcone O.—Following the procedure described in the previous section, 2-bromo-3,4,5-trimethoxybenzaldehyde was condensed with 3,4-dimethoxyacetophenone to give a 97% yield of the chalcone O, m.p. 126–137°, which was obtained in the form of pale yellow needles after four recrystallizations from methanol; m.p. 149–150°.

Anal. Calcd. for $C_{20}H_{21}BrO_6$: C, 54.93; H, 4.84. Found: C, 55.18; H, 5.16.

1-Keto-1-(3′,4′-dimethoxyphenyl)-3-(2′-bromo-3′,4′,5′-trimethoxyphenyl)-propane (Compound P).—Numerous attempts to reduce the chalcone O to the corresponding diarylpropane failed, the only isolable product being the ketone P, obtained as colorless blunt needles after several recrystallizations from petroleum ether (b.p. 63–69°); m.p. 93–94°.

Anal. Calcd. for $C_{20}H_{23}BrO_6$: C, 54.68; H, 5.28. Found: C, 55.08; H, 5.26.

The 2,4-dinitrophenylhydrazone of compound P was obtained, after several recrystallizations from ethanol-ethyl acetate, as brilliant red, feathery needles, m.p. 186–187°.

Anal. Calcd. for $C_{26}H_{27}BrN_4O_9$: C, 50.41; H, 4.39. Found: C, 50.74; H, 4.41.

2-(4′-Methoxyphenyl)-indan (IX).—Following a published procedure,[45] benzaldehyde was condensed with *p*-

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[39] R. L. Shriner and F. J. Wolf, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 737.

[40] *Cf.* J. Cason, *Chem. Rev.*, **40**, 15 (1947)

[41] F. E. King and T. J. King, *J. Chem. Soc.*, 726 (1942).

[42] K. Feist and G. L. Dschu, *Chem. Zentr.*, **98**, II, 58 (1927).

[43] H. R. Frank, P. E. Fanta and D. S. Tarbell, THIS JOURNAL, **70**, 2314 (1948).

[44] A. M. Hamburg, *Monatsh.*, **19**, 593 (1898).

[45] R. E. Buckles and E. A. Hausman, THIS JOURNAL, **70**, 415 (1948).

methoxyphenylacetic acid to give a 70% yield of α-(4'-methoxyphenyl)-cinnamic acid, m.p. 126–130°, which after one recrystallization had m.p. 157–158° (reported m.p. 152–153°).[46] The cinnamic acid was dissolved in dilute sodium hydroxide solution and hydrogenated with Raney nickel as catalyst to give 97% of β-phenyl-α-(4-methoxyphenyl)-propionic acid, m.p. 106–108° (reported[47] m.p. 108–109°). An 8.0-g. sample of the propionic acid was treated with anhydrous hydrogen fluoride to yield 4.5 g. (65%) of 2-(4'-methoxyphenyl)-indanone, b.p. 187–188° (0.5 mm.), which, after two recrystallizations from petroleum ether (b.p. 63–69°), was obtained as colorless, feathery needles, m.p. 84–85°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.86; H, 5.98.

The 2,4-dinitrophenylhydrazone of 2-(4'-methoxyphenyl)-indanone was obtained, after three recrystallizations from 95% ethanol, as red blades, m.p. 209–211°.

Anal. Calcd. for $C_{22}H_{18}N_4O_5$: C, 63.15; H, 4.34. Found: C, 63.16; H, 4.39.

A 4.0-g. sample of the crude indanone was dissolved in 50 ml. of ethyl acetate, treated with 0.5 g. of 10% palladium-on-charcoal catalyst and 15 drops of 70% perchloric acid, and hydrogenated at room temperature for 14 hr. at 2.5 atmospheres of pressure. The product was distilled through a 4-inch Vigreux column and consisted of 2.61 g. (69.5%) of a colorless oil, b.p. 138–141° (0.5 mm.), n^{25}D 1.5860.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.70; H, 7.26.

A diacetyl derivative of IX was prepared by the action of acetyl chloride and aluminum chloride in carbon disulfide solution. The product, obtained after several recrystallizations from ethyl acetate–petroleum ether (b.p. 63–69°), consisted of colorless needles, m.p. 106–107°.

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.61; H, 6.27.

2-(γ-Phenylpropyl)-benzonitrile (XV).—A 1.0-g. sample of 2-(γ-phenylpropyl)-benzaldehyde (XXXIII) was converted to the oxime[48] and the oxime was dehydrated according to a published procedure[49] to yield an oil which was purified by chromatography on alumina. Elution with a 1:1 mixture of petroleum ether (b.p. 63–69°)-benzene gave the nitrile XV as an oil, n^{25}D 1.5678, $\bar{\nu}_{max}^{liq}$ 2240 cm.$^{-1}$; λ_{max}^{EtOH} (ε) 214 mμ (14,500), 227 mμ (10,600), 276 mμ (1720), 285 mμ (1735).

Anal. Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83. Found: C, 86.68; H, 6.73.

2-(γ-Phenylpropyl)-toluene (Compound B).—A 6.0-g. sample of 2-(γ-phenylpropyl)-benzoic acid (XXIV) was dissolved in 100 ml. of dry ether and slowly added to a solution of 2.0 g. of lithium aluminum hydride in 100 ml. of dry ether. After an hour of refluxing, the mixture was processed to give 4.4 g. (94%) of compound A as a nearly colorless oil. This material was dissolved in ethyl acetate, treated with 0.3 g. of 10% palladium-on-charcoal catalyst and 1 ml. of perchloric acid, and hydrogenated at room temperature for 12 hr. at 2.5 atmospheres of pressure. The product was obtained in almost quantitative yield as a colorless oil, n^{26}D 1.5552.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.01; H, 8.73.

A diacetyl derivative of compound B was prepared by the action of acetyl chloride and aluminum chloride in carbon disulfide solution. The product was an oil and was converted to the 2,4-dinitrophenylhydrazone of the diacetyl derivative of B which was obtained, after several recrystallizations from ethyl acetate, as brick red crystals; m.p. 244–245°.

Anal. Calcd. for $C_{32}H_{28}N_8O_8$: C, 58.89; H, 4.32. Found: C, 58.78; H, 4.31.

1,2,4,5-Dibenzocycloöctadiene (Compound C).—2,3,6,7-Dibenzocycloöctadienone was prepared in 20% yield as an impure solid[50] from which a 2,4-dinitrophenylhydrazone was obtained as dull red plates crystallizing from ethyl acetate; m.p. 184–186°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51. Found: C, 65.85; H, 4.64.

Wolff–Kishner reduction of the ketone gave a 25% yield of an oil, b.p. 141–145° (0.5 mm.) and n^{25}D 1.6081, which solidified on standing, m.p. 135–136°. This material was converted to a diacetyl compound, obtained as an oil, from which a 2,4-dinitrophenylhydrazone was prepared and crystallized several times from ethyl acetate; m.p. 234–236° dec.

Anal. Calcd. for $C_{32}H_{28}N_8O_8$: C, 58.89; H, 4.32. Found: C, 59.05; H, 4.36.

2-Benzylindan (XIV).—2-Benzylindanone,[51] prepared by the cyclization of dibenzylacetic acid with anhydrous hydrogen fluoride, was hydrogenated in the presence of 10% palladium-on-charcoal and perchloric acid to give 2-benzylindan as a colorless oil, b.p. 113° (0.3 mm.), n^{25}D 1.5772; λ_{max}^{EtOH} (ε) 213 mμ (18,000), 260 mμ (1135), 267 mμ (1530), 273 mμ (1665).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.55; H, 7.88.

A diacetyl derivative of 2-benzylindan was obtained as colorless needles after recrystallization from aqueous ethanol; m.p. 87–88°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 81.89; H, 6.73.

2-Phenyltetralin (XI).—Hydrogenolysis of 2-phenyltetralone[23] gave 2-phenyltetralin[52] as a colorless oil. **A diacetyl derivative of 2-phenyltetralin** was obtained as colorless needles after recrystallization from ethanol; m.p. 136–137°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 82.21; H, 7.15.

2-(4'-Methoxyphenyl)-1,2,3,4-tetrahydro-6,7,8-trimethoxynaphthalene (XII). (A) α-(4'-Methoxyphenyl)-β-(3,4,5-trimethoxybenzoyl)-propionitrile (XXXVI).—Following a published procedure[53] a 72.2-g. sample of 4'-methoxybenzal-3,4,5-trimethoxyacetophenone (XXV) was converted to 73.2 g. (94%) of a yellow powder, m.p. 142–144°, which was obtained as colorless needles after recrystallization from ethanol; m.p. 144–145°, $\bar{\nu}_{max}^{CHCl_3}$ 1680, 2230 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{21}NO_5$: C, 67.59; H, 5.96. Found: C, 68.10; H, 6.25.

The 2,4-dinitrophenylhydrazone of XXXVI was obtained, after several recrystallizations from ethanol, as feathery, yellow-orange needles, m.p. 155.5–156°.

Anal. Calcd. for $C_{26}H_{25}N_5O_8$: C, 58.31; H, 4.71. Found: C, 57.87; H, 4.51.

(B) α-(4'-Methoxyphenyl)-β-(3,4,5-trimethoxybenzoyl)-propionic Acid (XXXVIII).—Following the procedure of Wenner[54] an 84-g. sample of XXXVI was hydrolyzed with concentrated hydrochloric acid followed by dilute hydrochloric acid to yield 56 g. (64%), after crystallization from ethanol, of nearly colorless needles, m.p. 173–174°. An analytical sample was obtained as colorless needles by further recrystallization from ethanol; m.p. 174–175°, $\bar{\nu}_{max}^{CHCl_3}$ 1680, 1710 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.46; H, 5.96.

The amide of XXXVIII was obtained as an intermediate in the above procedure as colorless needles after recrystallization from ethanol; m.p. 195–196°.

Anal. Calcd. for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21. Found: C, 64.22; H, 6.40.

(C) α-(4'-Methoxyphenyl)-γ-(3,4,5-trimethoxyphenyl)-butyric Acid (XLII).—A 28.0-g. sample of XXXVIII was dissolved in 250 ml. of glacial acetic acid, treated with 51 g.

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of 5% palladium-on-charcoal catalyst and 3 ml. of 70% perchloric acid, and hydrogenated for 22 hr. at 2.5 atmospheres of pressure. The product consisted of 27 g. (100%) of a greenish oil which was used, without purification, for the next step. An analytical sample was obtained as colorless rosettes by several recrystallizations from ether–petroleum ether (b.p. 63–69°); m.p. 79–95°, $\bar{\nu}_{max}^{CHCl_3}$ 1712 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 67.55; H, 6.95.

The benzylamine salt of XLII was obtained, after several recrystallizations from benzene–petroleum ether (b.p. 63–69°), as colorless needles, m.p. 110–111°.

Anal. Calcd. for $C_{27}H_{33}NO_6$: C, 69.36; H, 7.11. Found: C, 69.34; H, 6.83.

(D) **2-(4′-Methoxyphenyl)-3,4-dihydro-5,6,7-trimethoxynaphthalenone** (XL).—A 27.0-g. sample of XLII was heated for 25 min. at 95° with 150 ml. of polyphosphoric acid. The product consisted of 24.5 g. (96%) of a tan solid, m.p. 112–117°, which was recrystallized from benzene–petroleum ether (b.p. 63–69°) and obtained as colorless plates, m.p. 120–121°, $\bar{\nu}_{max}^{CHCl_3}$ 1680 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.58; H, 6.18.

The oxime of XL was obtained, after several recrystallizations from ethanol, as stout, colorless needles, m.p. 183–185°.

Anal. Calcd. for $C_{20}H_{23}NO_5$: C, 67.21; H, 6.49. Found: C, 66.87; H, 6.29.

(E) **2-(4′-Methoxyphenyl)-3,4-dihydro-6,7,8-trimethoxynaphthalene.**—A 7.0-g. sample of XL (m.p. 120–121°) was dissolved in 50 ml. of absolute methanol and treated at 25° over a period of 3 hr. with 2.4 g. of sodium borohydride. The product consisted of 6.4 g. (96%) of a white solid, m.p. 112–114°, which yielded colorless crystals after several recrystallizations from petroleum ether (b.p. 63–69°); m.p. 115–117°, λ_{max}^{EtOH} (ϵ) 241 mμ (14,000), 320 mμ (26,400).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.28; H, 6.63.

(F) **2-(4′-Methoxyphenyl)-1,2,3,4-tetrahydro-6,7,8-trimethoxynaphthalene** (XII).—Catalytic hydrogenation of 2-(4′-methoxyphenyl)-3,4-dihydro-6,7,8-trimethoxynaphthalene yielded XII as blunt, white needles after several recrystallizations from methanol; m.p. 81–82°; λ_{max}^{EtOH} (ϵ) 223 mμ (22,600), 277 mμ (2830), 283 mμ (2550).

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.46; H, 7.33.

2-(3′,4′-Dimethoxyphenyl)-1,2,3,4-tetrahydro-6,7,8-trimethoxynaphthalene (XIII). (A) **α-(3′,4′-Dimethoxyphenyl)-β-(3,4,5-trimethoxybenzoyl)-propionitrile (XXXVII).**—In the fashion indicated above, the chalcone XXVI was converted in 91% yield to a colorless powder, m.p. 143–145°, which gave colorless rosettes upon recrystallization from 95% ethanol; m.p. 144–145°.

Anal. Calcd. for $C_{21}H_{23}NO_6$: C, 65.44; H, 6.02. Found: C, 65.31; H, 5.75.

The 2,4-dinitrophenylhydrazone of XXXVII was obtained, after several recrystallizations from methanol, as brown plates, m.p. 196–197°.

Anal. Calcd. for $C_{27}H_{27}N_5O_9$: C, 57.34; H, 4.81. Found: C, 56.66; H, 4.77.

(B) **α-(3′,4′-Dimethoxyphenyl)-β-(3,4,5-trimethoxybenzoyl)-propionic Acid (XXXIX).**—Following the procedure previously indicated, the nitrile XXXVII was converted to the acid XXXIX in 53% yield, m.p. 194–196°. An analytical sample was obtained by further recrystallization from ethanol as colorless needles, m.p. 195–196°, $\bar{\nu}_{max}^{CHCl_3}$ 1680, 1710 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{24}O_8$: C, 62.37; H, 5.98. Found: C, 62.05; H, 5.84.

(C) **2-(3′,4′-Dimethoxyphenyl)-1,2-dihydro-6,7,8-trimethoxynaphthalenone** (XLI).—A 3.3-g. sample of the keto acid XXXIX was hydrogenolyzed to 3.1 g. (100%) of the reduced acid XLIII which was not isolated but used directly in the cyclization. A 3.1-g. sample of this material was mixed with 7 ml. of polyphosphoric acid and heated on the steam-bath for 30 min. The product consisted of 1.6 g. (57%) of a neutral oil from which the ketone was obtained as feathery needles after several recrystallizations from methanol; m.p. 141–142°, $\bar{\nu}_{max}^{CHCl_3}$ 1690 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.29; H, 6.27.

(D) **2-(3′,4′-Dimethoxyphenyl)-1,2,3,4-tetrahydro-6,7,8-trimethoxynaphthalene** (XIII).—A 0.500-g. sample of XLI was treated with 0.5 g. of 5% palladium-on-charcoal catalyst and 0.5 ml. of 70% perchloric acid and hydrogenated for 24 hr. at 2.5 atmospheres of pressure. The crude mixture was purified by chromatography on alumina and 0.125 g. of material was obtained which, after recrystallization from methanol, yielded XIII as colorless, blunt needles, m.p. 93–94°.

Anal. Calcd. for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 69.51; H, 7.10.

1-Keto-1-(4′-methoxyphenyl)-3-(2′-carboxy-3,4,5-trimethoxyphenyl)-propane (Compound R).—A 10.0-g. sample of the tetralone XL was refluxed for 5 hr. with 50 ml. of acetic anhydride to give 10.4 g. of a semi-solid product containing the enol acetate (compound Q), $\bar{\nu}_{max}^{CHCl_3}$ 1680, 1775 cm.$^{-1}$. This material, without purification, was dissolved in 50 ml. of chloroform and ozonized for 1.5 hr. at 0° in a stream containing 2% ozone. The acidic product consisted of 4.1 g. (37%) of a dark-colored oil which could not be induced to crystallize.

A 2,4-dinitrophenylhydrazone of compound R was obtained, after several recrystallizations from acetone, as brilliant red, very small crystals, m.p. 226–227°.

Anal. Calcd. for $C_{26}H_{26}N_4O_{10}$: C, 56.31; H, 4.73. Found: C, 56.21; H, 4.65.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Decomposition of Quaternary Aldehydes Derived from Morphine

BY HENRY RAPOPORT, ANDREW D. BATCHO AND JOHN E. GORDON[1]

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Morphine degradation products having a formyl group at C_{13} have been found to undergo free-radical decomposition with surprising ease. The product of this decomposition is the corresponding benzofuran, the 6,7,8,9,10,14-hexahydromorphenol methyl ether, and the formyl carbon appears as carbon monoxide. This reaction, coupled with glycol cleavage of the hydroxylated 13-vinyl compound, affords a procedure for stepwise removal of carbons 15 and 16 from morphine.

During work on some colchicine degradation products, the desirability arose of having some quaternary methoxyphenylacetaldehydes for comparison purposes. Such aldehydes had been prepared from codeine and isocodeine,[2] and had been characterized as their oximes. Since an appreciable amount of the 13-vinylhexahydromorphenol (IIIb) was at hand, its conversion to the desired aldehyde

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[1] National Science Foundation Fellow, 1953–1956.

[2] H. Rapoport and G. Payne, THIS JOURNAL, **74**, 2630 (1952).