

tograph. It could be applied to reaction periods of up to 32 min under the conditions employed.

Analysis of Products. Routine separations and quantitative determinations were carried out on an F and M Model 500 instrument with an 8 ft \times 0.25 in. od silica gel column, a temperature program covering the range 50–200° at 4° min⁻¹, and a helium flow rate of 30 cc min⁻¹. A typical chromatograph is shown in Figure 1. Retention times and area factors were determined with authentic samples. Areas were usually estimated by multiplying peak heights by their half-height widths. Separation of the nine products listed in Table II were clean except that propylene and allene overlapped, butane appeared as a tail-like shoulder on the cyanogen peak, and propyne was not completely separated from the single peak due to recovered butadiene plus *cis*-2-butene. These overlaps reduced the precision of determination of allene and propene, prevented quantitative estimation of butane by gas chromatography, and limited the ability to detect and determine propyne gas chromatographically to conditions where relatively little butadiene was recovered.

Acrylonitrile and acetonitrile could not be separated on silica

gel. They could be separated readily on diisodecyl phthalate and relative peak areas were determined on this absorbent. Area factors were not determined. Monomeric products were determined on Carbowax 20M as described previously.³

Propene was separated completely from allene and propyne from butadiene, both for purposes of infrared identification, by chromatographing on 8 ft of molecular sieve 5A, programmed from 200 to 250° at 5.6° min⁻¹.

A number of the less abundant products were isolated for infrared analysis from the products of runs carried out for several hours. A Perkin-Elmer Model 237 infrared spectrophotometer was used in conjunction with a 7.5-cm gas cell with NaCl windows to identify all products by comparison of spectra with those of authentic samples.

Materials. Nitrogen was Matheson "prepurified" grade (99.996%) further purified as described previously.⁸ 1,3-Butadiene was Matheson CP, purified by distilling on the vacuum line three times, discarding the first and last tenth each time. Nitric oxide was Matheson 99% purity distilled twice under vacuum at -131.5° (pentane slush).

Reactions Proceeding by the [3.2.1] Bicyclic Path¹

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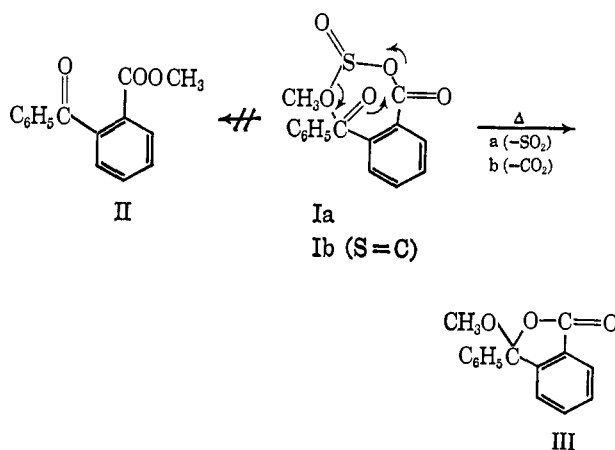
Contribution from the Evans Chemistry Laboratory of The Ohio State University, Columbus, Ohio 43210. Received October 8, 1965

Abstract: Pyrolysis of intermediates Ia and Ib affords pseudo- (ψ) methyl 2-benzoylbenzoate exclusively. Reaction of 2 moles of 2-benzoylbenzoic acid with 1 of ethoxyacetylene yields an intermediate (IX) which affords 2-benzoylbenzoic acid anhydride (X) shown to have the *n, ψ* structure instead of the *n,n* structure previously assigned. Reaction of 1 mole of 2-benzoylbenzoic acid with 1 of ethoxyacetylene yields 1-ethoxyvinyl 2-benzoylbenzoate (XV), which is rearranged to ethyl 3-phenylphthalide-3-acetate (XVI). The acid chloride of 2-benzoylbenzoic acid, however prepared, always has a cyclic structure. All of the above observations can be explained by the use of a [3.2.1] bicyclic path.

Since the discovery of a new reaction path does not occur frequently, the observations which led to the original experiments designed to test the hypothesis are of interest. The rate of alkaline hydrolysis of methyl 6-methyl-2-benzoylbenzoate had been found to be greater than that of methyl 2-benzoylbenzoate³ and the rate of acid-catalyzed esterification of 6-methyl-2-benzoylbenzoic acid with methanol had been found to be greater than that of 2-benzoylbenzoic acid.^{4,5} Both of these results were explained by mechanisms which involved attack of a reagent on the ketonic carbonyl rather than the carbonyl of the carboxy function.⁶ Since these reactions are intermolecular, the idea occurred that intramolecular reactions involving attack on the ketonic carbonyl might be discovered if suitable molecules were synthesized.

The first test of this idea involved the formation of an intermediate (Ia) by reaction of sodium 2-benzoylbenzoate with methyl chlorosulfite.⁷ On warming, Ia

could yield normal methyl 2-benzoylbenzoate (II) or the pseudo- (ψ) ester, III. Although the yield of ester was small (35%) in this experiment *only* ψ ester was formed. The formation of ψ ester could be formulated by an intramolecular attack, as shown, and thus a [3.2.1] bicyclic path seemed indicated. This encouraged, other reactions were tried and are described below.



(1) This research was supported by Grant GP-718 from the National Science Foundation.

(2) The material in this paper was taken from the thesis presented by C. C. to The Ohio State University, 1965.

(3) M. S. Newman and S. Hishida, *J. Am. Chem. Soc.*, **84**, 3582 (1962).

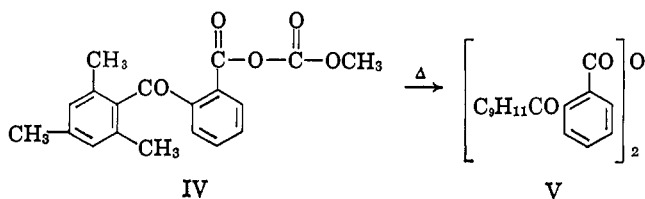
(4) M. S. Newman and C. Courduvelis, *ibid.*, **86**, 1893 (1964).

(5) M. S. Newman and C. Courduvelis, *J. Org. Chem.*, **30**, 1795 (1965).

(6) Other examples of such attacks are to be found in the papers of F. Ramirez, B. Hansen, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 4588 (1962), and of M. L. Bender and M. S. Silver, *ibid.*, **84**, 4589 (1962).

(7) M. S. Newman and W. S. Fones, *ibid.*, **69**, 1046 (1947), showed that sodium salts of acids react with *n*-butyl chlorosulfite to form intermediates which are converted to *n*-butyl esters on heating.

When 2-benzoylbenzoic acid was treated with methyl chlorocarbonate in the presence of Dabco,⁸ a crystalline intermediate (Ib) was obtained which, on heating at 100–120° for 20 min, yielded III (89%). We regard this as evidence for the [3.2.1] bicyclic path. Reaction by a competing mechanism, either four-centered or six-centered,⁹ which would have produced the normal methyl ester II did not interfere, as indicated by the absence of II in the product. When the intermediate IV, prepared from 2-(2',4',6'-trimethylbenzoyl)benzoic acid¹⁰ and methyl chlorocarbonate, was heated, no ester, pseudo or normal, was obtained. Instead a high yield of the n,n anhydride V resulted. (See below for a discussion regarding proof of structure.) This fact provides evidence that steric hindrance can prevent a reaction from taking place by the [3.2.1] bicyclic path.



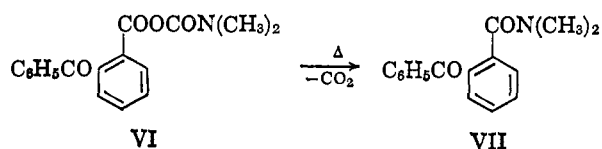
Another example of a reaction which might have occurred by the [3.2.1] bicyclic path but did not is provided by the fact that pyrolysis of N,N-dimethylcarbamic 2-benzoylbenzoic anhydride (VI) yields the di-

Table I. Ultraviolet Absorption Spectra

Compd	Wave-length, ^a m μ	Extinction coefficient
II	325	123
IV	325	133
V	332	438
VI	325	124
VII	330 ^b	133
X	325	128
XI	332	200
XII	344 ^c	186
XIII	344 ^c	450
XIV	325	145
XV	330	134

^a All spectra taken in chloroform using a Cary 14 instrument, except as otherwise noted. ^b Spectrum taken in methanol. ^c Spectra obtained on a Perkin-Elmer 202 instrument.

methylamide of 2-benzoylbenzoic acid (VII). The structure of VII was assigned on the basis of infrared and ultraviolet spectra (see Table I and discussion pertaining thereto).

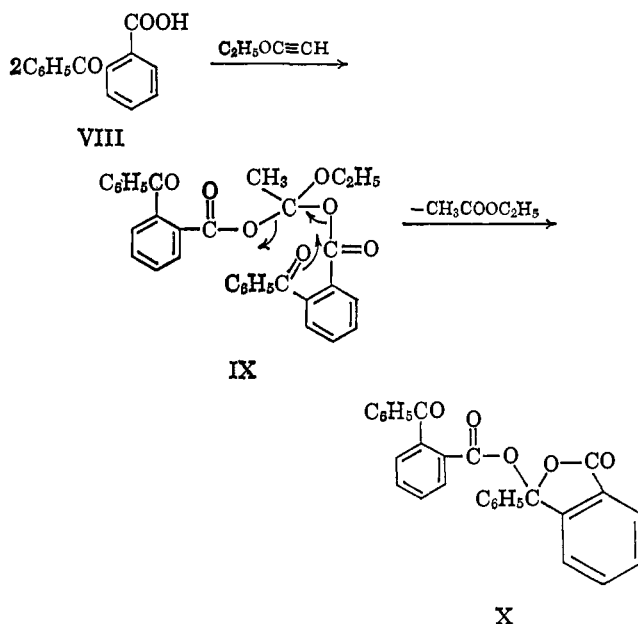


(8) 1,4-Diazabicyclo[2.2.2]octane. We thank the Houdry Process Co., Marcus Hook, Pa., for a generous sample of Dabco.

(9) See E. J. Longosz and D. S. Tarbell, *J. Org. Chem.*, **26**, 2161 (1961), and references therein for discussion of possible mechanisms for decomposition of mixed carboxylic-carbonic anhydrides.

(10) M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941).

The next example of reactions occurring by the [3.2.1] bicyclic path involved reactions of 2-benzoylbenzoic acid (VIII) with ethoxyacetylene. On treatment of VIII with ethoxyacetylene in methylene chloride at room temperature, the n, ψ anhydride X was obtained. This result is explained by assuming that 2 moles of VIII add to ethoxyacetylene to form the intermediate IX, which undergoes decomposition by the [3.2.1] path to yield X.



The formation of anhydrides from carboxylic acids and ethoxyacetylene¹¹ has been studied with the aid of O¹⁸ experiments.¹² The conclusion was drawn¹² that the mechanism involves a six-centered transition state, as postulated previously,¹³ rather than an ionic mechanism. In the case of VIII, however, the reaction proceeds by [3.2.1] bicyclic path, as shown, because the anhydride of VIII, mp 140°, obtained has the n, ψ structure (X) shown. Previously this anhydride was assigned the n,n structure on the basis of ultraviolet absorption in the 250–300-m μ region,¹⁴ and polarographic studies.¹⁵ Even if one argued that the n,n anhydride were formed first and then rapidly rearranged into the n, ψ anhydride X, the *rearrangement* would take place by the [3.2.1] path.

We have found that more accurate appraisals of normal and pseudo structures in the 2-benzoylbenzoic acid series can be made by measurements in the 320–350-m μ region,⁵ as compounds having the pseudo structure have almost no absorption in this region, while normal structures have (log ϵ 2+). Examination of the extinction coefficients in Table I reveals that the anhydride, X, of VIII has about the same ϵ value as does

(11) J. F. Arens, and P. Modderman, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **53**, 1163 (1950); *Chem. Abstr.*, **45**, 6152 (1951).

(12) H. H. Wasserman and P. S. Wharton, *J. Am. Chem. Soc.*, **82**, 1411 (1960).

(13) G. Eglinton, E. R. H. Jones, B. L. Shaw, and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954). Interestingly, the decomposition of the intermediate II formed from maleic acid and methoxyacetylene is pictured as taking place by a [3.2.1] bicyclic path. However, for steric reasons this path, in the case at hand, seems unlikely. Rather, the path is likely to be path A of ref 11 above.

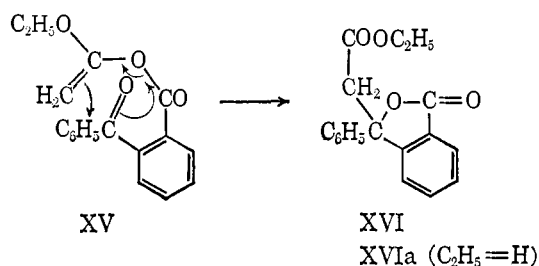
(14) H. Schmidt, M. Hochweber, and H. V. Halban, *Helv. Chim. Acta*, **31**, 354 (1948).

(15) S. Wawzonek and J. H. Fossum, *J. Electrochem. Soc.*, **96**, 234 (1949).

normal methyl 2-benzoylbenzoate (II) at 325 $m\mu$. However, if this anhydride had the normal-normal structure the ϵ value should have been at least double because of the *two* chromophores.¹⁶ To support this assumption, note that the ϵ value of V (Table I) is 438 whereas that of normal methyl 2-(2',4',6-trimethylbenzoyl)benzoate (XI) is 200. Also note the ϵ values of methyl 4-benzoylbenzoate (XII; 186) and of 4-benzoylbenzoic anhydride (XIII; 450). As a further check on our assignment of the n,ψ structure to X, we found that the absorption spectrum of an equimolar mixture of normal and pseudo methyl 2-benzoylbenzoates was almost identical with that of a solution of 1 equiv of X (all in chloroform).¹⁶

The same anhydride X was also prepared by: (a) treatment of 2-benzoylbenzoyl chloride (ψ structure, see below) with VIII and pyridine and (b) heating of the mixed anhydride, XIV, of VIII and acetic acid (n structure as postulated previously¹⁵).

In another experiment, 1 mole of 2-benzoylbenzoic acid was added to ethoxyacetylene as described¹⁷ to yield 1-ethoxyvinyl 2-benzoylbenzoate (XV) which was rearranged to ethyl 3-phenylphthalide-3-acetate (XVI) either by heat or by long standing at room temperature in the absence of moisture. The rearrangement of X to XVI is pictured as proceeding through a [3.2.1] bicyclic path. Thus, a new synthetic process is at hand.¹⁸ Hydrolysis of XVI afforded the corresponding acid (XVIa) after suitable treatment (see the Experimental Section); it proved to be identical with an authentic sample.¹⁹ Esterification of XVIa afforded XVI.



Finally, VIII was converted into the acid chloride by treatment with thionyl chloride at room temperature or by treatment of the sodium salt of VIII with thionyl chloride. In each case the crude acid chloride which had never been heated above room temperature had the same ultraviolet and infrared spectra as that of distilled acid chloride, XVIII. We picture these reactions as proceeding *via* a chlorosulfite anhydride (XVII), which decomposes readily through a [3.2.1] bicyclic path to XVIII, as shown.²⁰

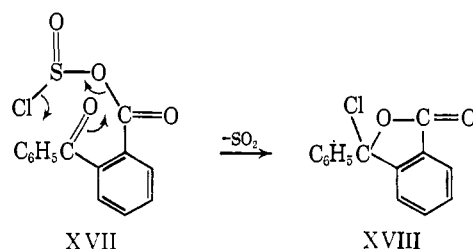
(16) Measurements in the 250–300- $m\mu$ region also confirmed the fact that the anhydride of VIII has the n,ψ structure. Interestingly, if one argued that the n,n anhydride were formed first and then rearranged to the n,ψ structure, the rearrangement would involve the [3.2.1] path.

(17) H. H. Wasserman and P. S. Wharton, *J. Am. Chem. Soc.*, **82**, 661 (1960).

(18) A lack of time prevented further study. However, more work is being done on this and similar reactions involving other acetylenic compounds.

(19) W. S. Johnson, A. L. McCloskey, and D. A. Dunnigan, *J. Am. Chem. Soc.*, **72**, 514 (1950). We thank Professor Johnson for sending us an authentic sample of XVIa.

(20) In other work here, levulinic acid has been shown to yield a cyclic acid chloride on similar treatment. We believe this fact makes unlikely a mechanism involving dissociation of the normal acid chloride into an acyclic acylium ion and a chloride ion, followed by cyclization to a lactonic carbonium ion and recombination of the latter with chloride ion to form the cyclic (ψ) acid chloride, because the tendency of



If very pure 2-benzoylbenzoic acid (VIII) is used and the product is carefully protected from moisture, the acid chloride²¹ can be vacuum distilled, whereupon it solidifies (mp 57–61°).²²

Experimental Section²³

Methyl Chlorosulfite. This compound, bp 39–40° (65 mm), was prepared in 92% yield as described²⁴ and kept sealed in ampoules until use (within 2 weeks of preparation).

ψ -Methyl 2-Benzoylbenzoate (III). **A. From Methyl Chlorosulfite.** To a magnetically stirred solution of 2.3 g of methyl chlorosulfite in 30 ml of dry ether was added a total of 5.0 g of powdered sodium 2-benzoylbenzoate in portions. After each addition a reaction occurred and the initial milkiness rapidly disappeared. Filtration 5 min after the last addition removed the sodium chloride. The solvent was removed in a rotary evaporator at room temperature. The oil remaining absorbed at 5.6, 5.8, and 6.0 μ . After heating at 110–130° for 1 hr, the product was worked up in the usual way. From the alkaline washings 1.6 g (36%) of VIII was recovered. A solution of the neutral product in carbon disulfide deposited 0.89 g (16%) of X,²¹ mp 140–141°. After removal of solvent from the filtrate crystallization from benzene-petroleum ether (bp 60–110°) afforded 1.8 g (35%) of III,²⁵ mp 78–81°.

B. From Methyl Chlorocarbonate. To a magnetically stirred solution of 6.78 g of VIII and 3.1 g of methyl chlorocarbonate²⁶ in 60 ml of dry ether at 0–5° was added a solution of 1.7 g of Dabco⁸ in 30 ml of ether during 30 min. After 1 hr at room temperature the colorless precipitate (water soluble) which had formed was removed by filtration. After the usual treatment of the filtrate, 6.9 g (80%) of Ib, mp 66–68°, infrared bands at 5.55, 5.78, and 6.02 μ , was obtained. Recrystallization from ether-petroleum ether did not change the melting point or infrared spectrum.

Anal. Calcd for C₁₅H₁₂O₅: C, 67.6; H, 4.2. Found: C, 67.5; H, 4.1.

Pyrolysis of 3.83 g of Ib near 120° showed that after 20 min gas evolution (CO₂) had ceased. The temperature was raised to 150° but no more gas evolution occurred. After the usual work-up an oil was obtained which crystallized on seeding with III to yield 2.88 g (89%) of III, mp 76–80°. The infrared spectrum was identical with that of pure III. The infrared spectrum of the oil residue from crystallization was essentially the same as that of III.

2-Benzoylbenzoic N,N-Dimethylcarbamic Anhydride (VI). A solution of 6.78 g of VIII, 3.6 g of N,N-dimethylcarbamyl chloride,²⁶ and 1.7 g of Dabco⁸ in 80 ml of ether was stirred at room temperature for 3.5 hr. After filtration of a precipitate, the filtrate was worked up as usual (5.13 g of VIII recovered from the alkaline wash) to yield 1.80 g (20%) of VI, mp 86–88°. Recrystallization

levulinic acid to form a lactonic carbonium ion should not be pronounced.

(21) Stated to be cyclic by A. Haller and A. Guyot, *Bull. Soc. Chim. France*, [3] **25**, 54 (1901).

(22) E. B. Hershberg, Ph.D. Dissertation, Massachusetts Institute of Technology, 1933, reports mp 60°.

(23) All melting points are uncorrected and were taken with standardized thermometers. Analyses by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Infracord. Identity of known compounds was always established by spectral comparisons and mixture melting point determinations. The phrase "worked up as usual" means that an ether-benzene solution of the products was washed with aqueous acid and/or alkali and saturated sodium chloride solution, and was filtered through anhydrous magnesium sulfate. The solvents then were removed on a rotary evaporator and the residue was treated as described. All experiments were repeated at least one time.

(24) G. Berti, *J. Am. Chem. Soc.*, **76**, 1213 (1954).

(25) H. Meyer, *Monatsh.*, **25**, 475 (1904).

(26) Used as received from the Aldrich Chemical Co.

from ether-petroleum ether yielded, with little loss, pure VI, mp 87–89°, infrared bands (in chloroform) at τ 5.62, 5.80, and 6.01 μ , nmr²⁷ bands at 2.61 (multiplet, 9 H, aromatic) and 7.22 (doublet, 6 H, $J = 6$ cps, CH_3NCH_3).

Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4$: C, 68.7; H, 5.0; N, 4.7. Found: C, 68.4; H, 4.9; N, 4.7.

Alternately, a 1:1 molar ratio mixture of potassium 2-benzoylbenzoate and *N,N*-dimethylcarbamoyl chloride in *N*-methylpyrrolidone²⁸ was heated at 130–140° for 3 hr, to give a 73% yield of a dark oil which had the same spectral properties as the pyrolysis product of VI prepared as described above. However, no purification of this product was attempted.

***N,N*-Dimethylamide of 2-Benzoylbenzoic Acid (VII).** Pyrolysis of 1.0 g of VI at 125° for 30 min and at 145° for 5 min afforded 0.76 g (90%) of VII, mp 78–80°, after the usual work-up and crystallization from ether. Recrystallization did not improve the melting point. No depression of the melting point was observed on mixing with a sample of VII prepared from 2-benzoylbenzoyl chloride, XVIII, and dimethylamine as described.²⁹ Pure VII had infrared bands at 6.02 and 6.12 μ and nmr bands at τ 2.48 (multiplet, 9 H) and 7.32 (singlet, 6 H).

2-(2',4',6'-Trimethylbenzoyl)benzoic Methylcarbonic Anhydride (IV). From the reaction of 2-(2',4',6'-trimethylbenzoyl)benzoic acid¹⁰ and methyl chlorocarbonate as described for the preparation of Ib there was obtained in 75% yield pure IV, mp 101–104°, infrared bands at 5.51, 5.70, and 6.02 μ . See Table I for ultraviolet data.

Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5$: C, 69.6; H, 5.5. Found: C, 70.1; H, 5.6.

2-(2',4',6'-Trimethylbenzoyl)benzoic Anhydride (V). When pure IV was pyrolyzed at 125° for 15 hr the anhydride V, mp 156–158°, infrared bands at 5.50, 5.76, and 5.98 μ , nmr bands at τ 7.85 and 8.17 in the ratio 1:2 for the methyl groups, was obtained in 79% yield (68% high purity). A benzene solvate, mp 164–166°, was obtained on recrystallization from benzene. The *n,n* structure of V was deduced from the ultraviolet absorption, (see Table I).

Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_5$: C, 78.8; H, 5.8. Found: C, 79.0; H, 5.9.

2-Benzoylbenzoic Anhydride (X). A solution of 11.33 g of VIII and 1.75 g of ethoxyacetylene³⁰ in 100 ml of dry methylene chloride was stirred at room temperature for 30 min. After the usual work-up an 85% yield of crude X, mp 138–141°, was obtained (10% of VIII recovered from alkaline wash). Recrystallization from benzene-petroleum ether afforded 8.25 g (75%) of pure X, melting point and mixture melting point with a sample prepared as described,³¹ 141–142°. The intermediate mixed anhydride of VIII

and acetic acid had no absorption above 300 $m\mu$ and hence has the ψ structure as previously postulated.¹⁵

Methyl 4-Benzoylbenzoate (XIII). This ester, mp 107–108°, was prepared by esterification of 4-benzoylbenzoic acid,³² mp 194–197°.

4-Benzoylbenzoic Anhydride (XIV). To a stirred suspension of 11.3 g of 4-benzoylbenzoic acid in 300 ml of benzene at 40° was added a solution of 1.75 g of ethoxyacetylene³⁰ in 10 ml of dry benzene. After 3 hr at 40° the mixture was worked up as usual to yield 67% of pure XIV, mp 174–177°, infrared bands at 5.60, 5.79, and 6.07 μ .

Anal. Calcd for $\text{C}_{28}\text{H}_{18}\text{O}_5$: C, 77.4; H, 4.1. Found: C, 77.2; H, 4.1.

1-Ethoxyvinyl 2-Benzoylbenzoate (XV). To a stirred solution of 7.7 g of ethoxyacetylene³⁰ and 0.4 g of mercuric acetate in 120 ml of dry methylene chloride cooled by a Dry Ice-acetone bath was added a solution of 11.3 g of VIII in 100 ml of methylene chloride during 30 min. After the mixture had reached room temperature the mixture was worked up as usual to yield 14.6 g (99%) of crude XV, mp 68–72°. Recrystallization from benzene-petroleum ether afforded pure XV, mp 72–74°, infrared bands appearing at 5.75, 5.98, and 6.03 μ , nmr bands at τ 2.50 (multiplet, 9 H, aromatic), 6.43 (quartet, 2 H, CH_2O), 6.50 (singlet, 2 H, $\text{CH}_2=$), and 8.80 (triplet, 3 H, CH_3).

Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4$: C, 73.0; H, 5.4. Found: C, 73.0; H, 5.4.

When XV is exposed to moisture for a time it is converted into X.

Ethyl 3-Phenyl-3-phthalideacetate (XVI). In a run in which 12.0 g of XV was prepared as described above, the crude product, mp 72–74°, was left in a flask protected from moisture for about 4 weeks. During this time the solid slowly liquefied and after 4 weeks was completely noncrystalline. On scratching the oil solidified. Recrystallization from benzene-petroleum ether yielded 2.85 g (66%), of solid, mp 91–94°. This material showed no depression in melting point when mixed with a sample of XVI made by treating the corresponding acid¹⁹ (XVIa) with thionyl chloride and the acid chloride thus produced with ethanol. Both samples of ester gave the same infrared spectrum, bands at 5.71 and 5.80 μ , and nmr spectrum, bands at τ 2.55 (multiplet, 9 H aromatic), 6.10 (quartet, 2 H, CH_2O), 6.57 (singlet, 2 H, CH_2), and 9.00 (triplet, 3 H, CH_3).

When 9.8 g of crude XV was distilled at 1.4 mm, 7.2 g, bp 205–220°, was obtained. On crystallization the distillate yielded 4.9 g (50%) of slightly yellow XVI, mp 86–90°, which was shown to be essentially identical with the material described above. In other heating experiments at 170–175°, about 1.5 hr was required for complete rearrangement as indicated by infrared spectral measurements. On heating for longer times, the yield of XVI decreased. More work is needed in this area.

On alkaline hydrolysis (3 hr in aqueous methanolic sodium hydroxide) an acid material was obtained which after boiling in 20% hydrochloric acid suspension for 1 hr yielded an acid, mp 174–179°, which showed no depression of melting point when mixed with an authentic sample¹⁹ of XVIa, infrared bands appearing at 5.68 and 5.82 μ .

(32) E. Wertheim, *J. Am. Chem. Soc.*, **55**, 2540 (1933).

(27) We acknowledge with gratitude the use of Varian Associates A-60 nmr instrument purchased by O. S. U. with an equipment grant from the National Science Foundation. Tetramethylsilane was used as standard.

(28) We thank the Antara Chemicals for a generous gift of this reagent.

(29) H. W. Bersch, K. H. Fischer, and V. Banniza, *Arch. Pharm.*, **294**, 601 (1961).

(30) Used as obtained from the Pfister Chemical Co., Ridgefield, N. J.

(31) H. F. von Pechmann, *Ber.*, **14**, 1865 (1881).