Reactions Proceeding by Bicyclic Mechanisms[1]

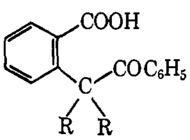
Melvin S. Newman, Slobodan Mladenovic,[2a] and Lekhu K. Lala[2b]

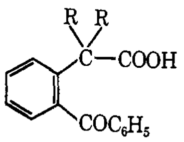
Contribution from the Evans Chemistry Laboratory, The Ohio State University, Columbus, Ohio 43210. *Received August 3, 1967*

Abstract: Pyrolysis of the mixed anhydrides of methylcarbonic acid with *o*-(α,α-dimethylphenacyl)benzoic acid and *o*-benzoyl-α,α-dimethylphenylacetic acid have been studied. Some of the reactions involved may be explained by postulating [3.3.1]bicyclic mechanisms. Pyrolyses of the mixed anhydride of methylcarbonic and *o*-phenacylbenzoic acids and of 1-ethoxyvinyl *o*-phenacylbenzoate to yield 3-phenylisocoumarin are explained by postulation of a [4.2.2]bicyclic path.

In earlier work certain reactions involving *o*-benzoylbenzoic acid[3] and levulinic acid[4] derivatives were explained by assuming [3.2.1]bicyclic mechanisms. Since these reactions involve γ-keto acids, we were interested to see if analogous reactions would take place with δ-keto acid derivatives.

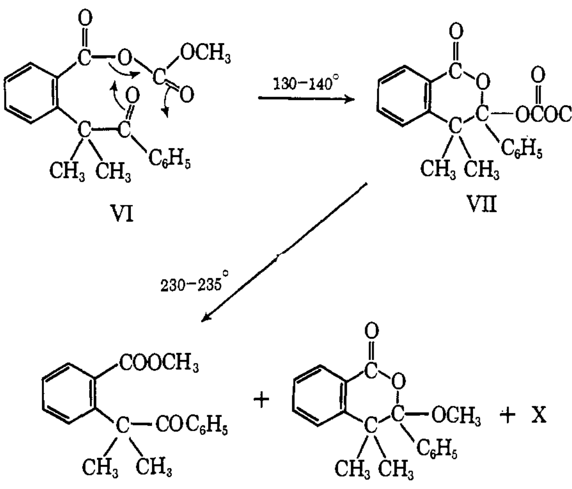
In this paper we describe experiments involving four such acids: *o*-(α,α-dimethylphenacyl)benzoic acid (I, R = CH_3),[5] *o*-benzoyl-α,α-dimethylphenylacetic acid (II, R = CH_3),[6] *o*-phenacylbenzoic acid (III, R = H),[5,7] and *o*-benzoylphenylacetic acid (IV, R = H).[6]


I, R = CCH_3
III, R = H


II, R = CH_3
IV, R = H

Since one reaction studied involved pyrolysis of the mixed anhydrides of these acids with methylcarbonic acid, we prepared the comparable mixed anhydride of *o*-toluic acid (V) to learn something of the thermal stability of a mixed carbonic anhydride which does not contain an additional ketonic function. This compound was stable when heated at 100–110° but decomposed quantitatively to methyl *o*-toluate and carbon dioxide on heating to 150–160°.

When VI, the mixed anhydride of I and methylcarbonic acid, was heated at 130–140° rearrangement to VII in high yield occurred.[8] This rearrangement is pictured as proceeding *via* a [3.3.1]bicyclic path. On heating VII to higher temperatures no reaction occurred until temperatures in the region of 230–235° were attained when decomposition to yield the normal methyl ester VIII, the pseudo methyl ester IX, and an anhydride mixture X in about 30–35% yield, each, took place.[9] Possibly the formation of VIII from VII involves a [3.3.1]bicyclic path with loss of carbon dioxide.



VI
VII
VIII
IX

The anhydride mixture proved to be difficult to separate into pure components. Hence we do not assign any specific structures to the components at present. Undoubtedly some cyclic anhydride (similar to pseudo ester) is present as judged by nmr studies which show some nonequivalent methyl groups (in the *gem*-dimethyl area).

When XI, the mixed anhydride of II and methylcarbonic acid, was prepared by treatment of the sodium salt of II with methyl chlorocarbonate, care had to be taken to keep the reaction mixture at 0–5° (also during the work-up) in order to show the presence of the acyclic anhydride XI. On standing at room temperature in ether solution, XI rearranges completely to the cyclic anhydride XII. This rearrangement is pictured as proceeding *via* a [3.3.1]bicyclic mechanism similar to that used to account for the rearrangement of VI to VII. Examination of molecular models reveals a likely explanation for the greater ease of rearrangement of XI to XII than that of VI to VII: there is a greater relief of strain in the former case.

On heating XII at 170° for 45 min a mixture of 80% pseudo ester XIII and 20% anhydride XIV is obtained. If the pyrolysis temperature is 230°, 55–60% XIII and 40–45% XIV are formed. The failure to obtain any normal methyl ester of *o*-benzoyl-α,α-dimethylphenylacetic acid (II) in the pyrolysis of XII (as contrasted to the formation of VIII in the pyrolysis of VII) may be

---

[1] This research was supported by a grant from the U. S. Army Research Office, Durham, N. C.

[2] (a) Postdoctoral Research Assistant, 1965–1966. (b) Postdoctoral Research Assistant, 1966–1967.

[3] (a) M. S. Newman and C. Courduvelis, *J. Amer. Chem. Soc.*, 88, 781 (1966). (b) See M. S. Newman and L. K. Lala, *J. Org. Chem.*, 32, 3225 (1967), for correction of one type of reaction described in ref 3a.

[4] M. S. Newman, N. Gill, and B. Darre, *J. Org. Chem.*, 31, 2713 (1966).

[5] M. Renson and L. Christiaens, *Bull. Soc. Chim. Belges*, 71, 394 (1962).

[6] M. Renson and L. Christiaens, *ibid.*, 379 (1962).

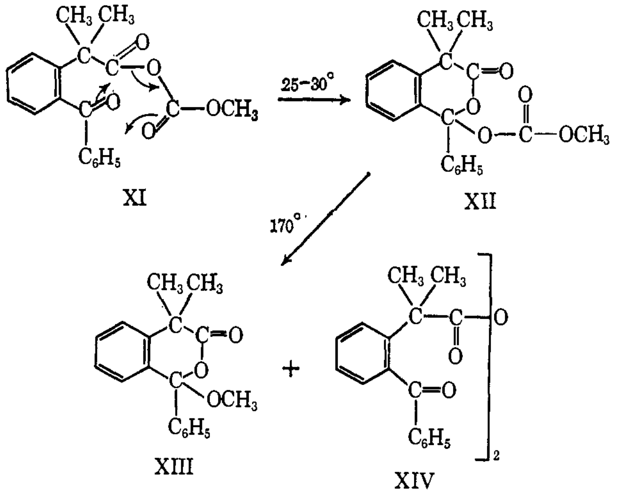
[7] C. Graebe and F. Trumpy, *Ber.*, 31, 375 (1898).

[8] See M. S. Newman and S. Mladenovic, *J. Amer. Chem. Soc.*, 88, 4523 (1966).

[9] This result does not agree with that described in the preliminary communication[8] in which only the formation of IX was described. We cannot account for the difference in results but the results herein reported have been repeated several times.

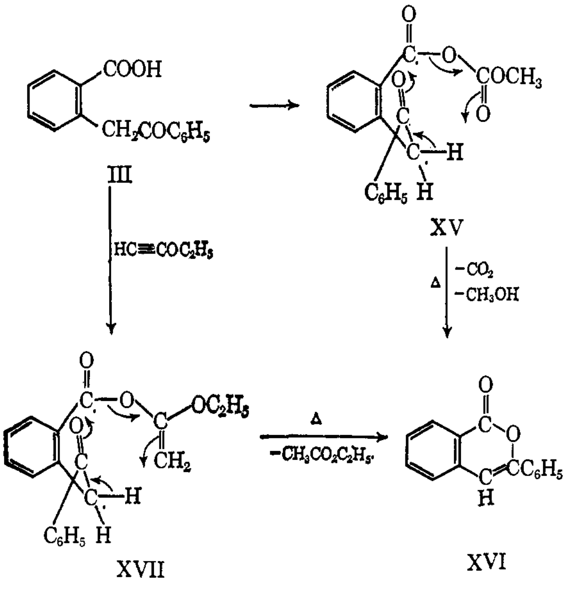
explained by assuming that there is greater strain in the [3.3.1]bicyclic path leading to formation of normal ester and hence the formation of XIII and XIV is preferred. The fact that the anhydride XIV formed has the normal–normal structure is surprising. We have no explanation to offer for its formation at this time. We have not studied this type of pyrolytic cleavage reaction further.[10]

In conclusion, it should be emphasized that new reactions have been described which may be explained by postulating [3.3.1]- and [4.2.2]bicyclic mechanisms. Further work to explore the generality of these reactions in the aliphatic field is contemplated.

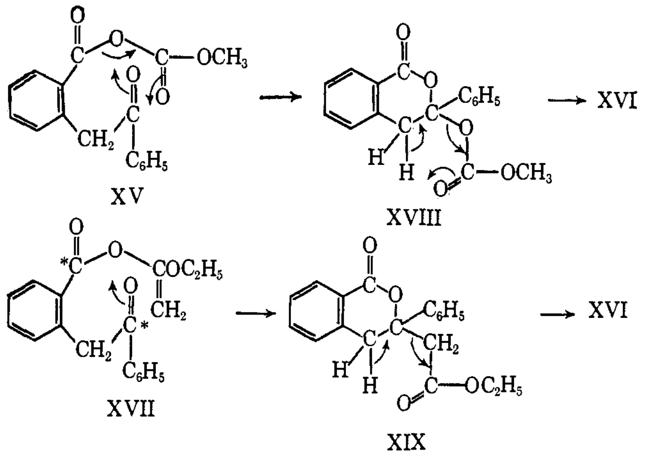


Before working with I and II we prepared *o*-phenacylbenzoic acid (III) and *o*-benzoylphenylacetic acid (IV) as model compounds for study of reactions which might take place by [3.3.1]bicyclic paths. However, competing side reactions described below prevented the studies we had planned.

Treatment of III with methyl chlorocarbonate in the presence of Dabco,[11] or of the sodium salt of III with the same reagent, afforded the acyclic mixed anhydride XV in high yield. At temperatures of 70–80° (both neat and in inert solvents) XV is stable, but on heating to 100–110° it affords 3-phenylisocoumarin[7,12] in 95% yield. Similarly, when III was added at −50° to ethoxyacetylene containing mercuric acetate a high yield of the vinyl ether XVII was obtained which on heating to 80° readily yielded XVI and ethyl acetate (compare ref 3a). However, when ethoxyacetylene was added to 2 equiv of III at −70°, and the temperature of the reaction mixture was allowed to rise to room temperature, a 75% yield of the normal–normal anhydride of III was obtained.



Since the decompositions of XV and XVII occur under such similar conditions most likely they occur by similar mechanisms, namely the [4.2.2]bicyclic path shown on the formulas (the starred carbons in formulas XV and XVII are the bridgehead carbons for the [4.2.2] path). Alternately one can depict the decompositions of XV and XVIII to occur in two steps as shown below. In the first step XV rearranges to XVIII and XVII to XIX *via* [3.3.1]bicyclic paths, followed by six-atom cyclic decompositions of XVIII and XIX to XVI. In the cases of the [3.3.1] paths shown below note that different bridgehead carbons are involved. However, since the decomposition of XIX as shown would involve the cleavage of a carbon–carbon bond at a temperature as low as 80°, we rule out the two-step sequence for XVII to XVI, and hence by analogy we argue that the rearrangement of XV to XVI does not involve XVIII. Inspection of models reveals that the [4.2.2] path is readily attained. A mechanism involving enolization of the carbonyl group of XV (or XVII) followed by lactonization to yield XVI can also be involved. However, since the reactions were carried out in specially cleaned apparatus and pure solvents were used, the likelihood of enolization is reduced.



These reactions do not take place by free-radical chain mechanisms as judged by the fact that they occur as readily in the presence of iodine as in its absence.

Treatment of *o*-benzoylphenylacetic acid (IV) with methyl chlorocarbonate and Dabco resulted in the formation in high yield of a red oil which resisted attempts at purification. However, we believe that this oil was essentially the mixed anhydride of *o*-benzoylphenylacetic acid and methyl carbonic acid (XX) as

---

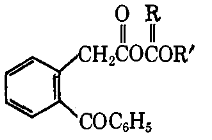
(10) Professor R. Augustine, Seton Hall University, South Orange, N. J., has informed us that he is studying the pyrolysis of mixed anhydrides of this type. Because of crossover results in studies involving reactions similar to the rearrangement of VI to VII and of XI to XII, he has shown that this type of reaction is intramolecular. His results will be reported shortly in conjunction with other work in this area.

(11) Dabco is 1,4-diazabicyclo[2.2.2]octane. We thank the Houdry Process Company, Marcus Hook, Pa., for a generous sample.

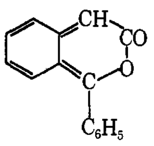
(12) S. Gabriel, *Ber.*, 18, 2445 (1885); R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 28, 3313 (1963).

indicated by the nmr and ir spectra. On heating to 100–110°, carbon dioxide and methanol were produced, and a red oil was obtained. This red oil was mainly polymeric. All attempts to trap the expected monomeric product XXI by the use of maleic anhydride or vinylene carbonate[13] failed. A similar product formed by treatment of IV with thionyl chloride has been described.[6]

When IV was added to ethoxyacetylene at −70° a red oil was obtained in high yield. Again, all attempts to obtain a pure sample failed, but nmr and ir spectra indicated that this oil was essentially the ethoxyvinyl *o*-benzoylphenylacetate (XXII). On heating XXII to 140° ethyl acetate was produced and a polymeric oil similar to that described above was formed.



XX, R = O; R′ = CH_3
XXII, R = CH_2; R′ = C_2H_5



XXI

To summarize our work, we have presented evidence that certain reactions occur by novel bicyclic mechanisms. The work to date does not firmly establish the mechanisms proposed but does make a sufficiently strong case in their favor that they must be carefully considered. The reactions evidently do not take place by free-radical chain mechanisms as they occur just as readily in the presence of iodine.

All of the structures of the new compounds herein reported have been established by analytical and spectroscopic methods which are described in the Experimental Section. One interesting feature of the nmr spectra is that the methyl groups of the *gem*-dimethyl groupings show a sharp singlet in compounds having an acyclic structure whereas in the cyclic forms the methyl groups appear as two separate singlets because of the different environments of each.

Experimental Section[14]

Mixed Anhydride of *o*-(α,α-Dimethylphenacyl)benzoic Acid and Methylcarbonic Acid (VI). To a suspension of the sodium salt of 0.01 mol of I in 250 ml of dry ether at 0–5° was added dropwise during 1 hr 1.0 g of pure methyl chlorocarbonate. After standing 12 hr at room temperature the material was worked up as usual[14] to yield 3.06 g (92%) of colorless crystalline VI, mp 85–88°; ir bands at 5.46, 5.65, 5.82; nmr bands at 1.78 (singlet, 6 H, CH_3 on C), 3.87 (singlet, 3 H, O–CH_3).

Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.9; H, 5.6. Found: C, 70.1; H, 5.7.

The same compound was obtained in comparable yield when the acid I was allowed to react with methyl chlorocarbonate in ether containing Dabco.

3,4-Dihydro-3-hydroxy-4,4-dimethyl-3-phenylisocoumarin, Methyl Carbonate (VII).[15] On heating molten VI for a short time at 130–135° solidification occurred. Recrystallization from benzene-Skellysolve B[16] afforded pure VII, mp 219–223° dec, ir bands at 5.67 and 5.77; nmr bands, two singlets, 3 H each, at 1.18 and 1.56 for the C-methyl groups, 3.65 (singlet, 3 H, O–CH_3).

Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.9; H, 5.6. Found: C, 69.7; H, 5.6.

Methyl *o*-(α,α-Dimethylphenacyl)benzoate (VIII) and 3,4-Dihydro-3-methoxy-4,4-dimethyl-3-phenylisocoumarin (IX). On heating 1 g of VII at 230–235° for about 45 min a mixture of products is obtained which consists of about 30% of VIII, 30% of IX, and about 35% of a mixture of the anhydrides of *o*-(α,α-dimethylphenacyl)benzoic acid (Xa and Xb) (see below). The compounds VIII and IX were separated from the anhydrides Xa and Xb by taking advantage of their ready solubility in methylene chloride-hexane. The proportion of VIII and IX was determined as about equal by nmr analysis since the *gem*-dimethyl groups in pure VIII[17] give a singlet band at 1.76 whereas in the pseudo ester IX there are two singlets for these methyl groups at 1.21 and 1.48. A check point is provided by the OCH_3 band in VIII at 3.49 and the OCH_3 band in IX at 3.13. Pure VIII is a liquid and pure IX[5] melts at 173–174°. They were separated by chromatography.

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4. Found (VIII): C, 76.6; H, 6.4.

***o*-Benzoyl-α,α-dimethylphenylacetic Acid (II).** The synthesis of this acid was improved in several steps. The condensation of acetone with diethyl malonate to yield diethyl isopropylidenemalonate was effected in 66% yield (lit.[18] 52%) by increasing the reflux time to 48 hr. The 1,4 addition of phenylmagnesium bromide to the above ester was improved to 70% (lit.[19] 40%) by the addition of cuprous chloride[20] to the Grignard reagent. Hydrolysis of the 1,4 addition product followed by decarboxylation of the malonic acid yielded 3-methyl-3-phenylbutyric acid[19] which was cyclized to 3,3-dimethyl-1-indanone as described.[21] The reaction of this indanone with phenylmagnesium bromide and dehydration of the resulting tertiary alcohol were done essentially as described[22] to yield 3,3-dimethyl-1-phenylindene. The oxidation of the latter to II was improved over that described (18%[5]) as follows. A solution of 80.0 g of CrO_3 in 500 ml of acetic acid was added slowly to a solution of 30 g of the indene in 100 ml of acetic acid, the temperature being held at 0–5°. After the exothermic reaction was over the mixture was stirred at room temperature for 24 hr and then poured into 1 l. of water. The ether-benzene extract of this mixture was washed with water and then K_2CO_3 solution. Acidification of this extract yielded crude acid, 197–201°, in 96% yield. Recrystallization from chloroform-hexane afforded 32 g (90%) of pure II, mp 201–203°.

1-Hydroxy-4,4-dimethyl-1-phenyl-3-isochromanone, Methyl Carbonate (XII). To a stirred mixture of 1.34 g of II and 0.5 g of methyl chlorocarbonate in 40 ml of dry ether was added 0.3 g of Dabco. After stirring overnight at room temperature, the precipitate was filtered and the filtrate worked up as usual to yield 1.45 g (89%) of XII, mp 130–132°, ir band, broad peak near 5.72; nmr band at 1.52 (singlet, 3 H, CH_3), 1.76 (singlet, 3 H, CH_3), 3.67 (singlet, 3 H, OCH_3).

Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.9; H, 5.6. Found: C, 70.0; H, 5.5.

The same compound was obtained in 82% yield when a mixture of the sodium salt of II and methyl chlorocarbonate was stirred for 10–12 hr at room temperature. In a comparable experiment in which the mixture was stirred at 0–5° and the work-up executed rapidly at low temperatures, a product was obtained which appeared to be a mixture of XI and XII, as judged by nmr bands at 1.78 (singlet, 3 H, CH_3 acyclic), 1.74 (singlet, 3 H, CH_3), 1.51 (singlet,

---

[13] M. S. Newman and R. Addor, *J. Amer. Chem. Soc.*, **77**, 3789 (1955).

[14] The term "worked up in the usual way" means that a solution of the reaction products in a water-immiscible solvent was washed with dilute acid and/or alkali, then with saturated sodium chloride solution. This solution was then filtered through anhydrous magnesium sulfate and the solvent removed, usually on a rotary evaporator. All experiments involving pyrolysis were conducted in glass apparatus that had been steamed out for 20 min to ensure that no acid was absorbed on the surface. All solvents were carefully purified before use. All microanalyses were by the Galbraith Microanalytical Laboratory, Knoxville, Tenn. All nmr bands are in parts per million relative to tetramethylsilane. All ir bands are in μ. All uv bands are in mμ.

[15] We thank Dr. K. Loening, *Chemical Abstracts*, for help in naming compounds.

[16] Petroleum ether, bp 65–70°.

[17] In ref 5 the preparation of VIII by treatment of I with diazomethane was reported. The oily product was not analyzed or otherwise characterized.

[18] A. C. Cope and E. M. Hancock, *J. Amer. Chem. Soc.*, **60**, 2644 (1938).

[19] F. S. Prout, E. Haung, R. J. Hartman, and C. J. Korpics, *ibid.*, **76**, 1911 (1954).

[20] J. Munch-Petersen, *J. Org. Chem.*, **22**, 170 (1957).

[21] K. Ninomiya and Y. Tamura, *J. Pharm. Soc. Jap.*, **76**, 163 (1956).

[22] C. F. Koelsch and P. P. Johnson, *J. Amer.Chem. Soc.*, **65**, 567 (1943); E. Bergmann, H. Taubadel, and H. Weiss, *Ber.*, **64**, 1493 (1931).

3 H, CH$_3$), 3.79 (singlet, 3 H, OCH$_3$ acyclic), 3.67 (singlet, 3 H, OCH$_3$ cyclic).

When XII was heated at 175–180° for 45 min, a mixture containing the pseudo methyl ester XIII and the bis-normal anhydride of II, namely XIV, in the ratio of 4:1 was produced. When the pyrolysis temperature was about 230°, there was produced about 55-60% XIII, mp 119-120°, and 40–45% XIV, mp 145-146°. The pseudo methyl ester XIII was identical with an authentic sample[6] produced from II. The anhydride XIV was assigned the *n-n* structure on the basis of analysis, hydrolysis to yield II, the fact that the nmr spectrum gave a singlet at 1.7 for all of the methyl hydrogens, and the uv spectrum consisted of a band at 252 (ϵ 32,500) whereas the normal methyl ester of II absorbs at 251 (ϵ 13,500).[23]

Anal. Calcd for $C_{32}H_{30}O_5$: C, 78.7; H, 5.8. Found: C, 78.4; H, 5.8.

1-Acetoxy-4,4-dimethyl-1-phenyl-3-isochromanone. A solution of 1.34 g of II in 10 ml of acetic anhydride was refluxed overnight. Acetic anhydride was removed under vacuum to give 1.49 g (97%) of anhydride, mp 131–135°. Recrystallization from chloroform-hexane yielded a pure sample, mp 135–137°, ir band at 5.69; nmr bands at 1.61 (singlet, 3 H, C–CH$_3$), 1.80 (singlet, 3 H, C-CH$_3$), 2.05 (singlet, 3 H, O═C—CH$_3$).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 74.0; H, 5.8. Found: C, 74.0; H, 5.6.

o-**Phenacylbenzoic Acid** (III). To a stirred solution of 8.1 g of homophthalic anhydride[24] in 300 ml of benzene was added 15.5 g of anhydrous aluminum chloride all at once. The mixture was slowly heated to reflux, held there for 4.5 hr, and poured on ice and hydrochloric acid. The washed organic product was taken into alkali. Acidification afforded III,[5] mp 165-167°, in 97% yield. On treatment of III in ether with diazomethane, a quantitative yield of methyl *o*-phenacylbenzoate,[25] mp 110–112°, ir bands at 5.91, and 6.01, was obtained.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.5; H, 5.5. Found: C, 75.6; H, 5.6.

Mixed Anhydride of *o*-**Phenacylbenzoic and Methylcarbonic Acids** (XV). To a solution of 2.40 g of III in about 250 ml of dry ether at 0–5° was slowly added 1.04 g of methyl chlorocarbonate. After addition of 0.56 g of Dabco to this solution in the cold and stirring at room temperature for 2 hr, the mixture was filtered. The filtrate was extracted with sodium carbonate (acidification of which returned 10–15% of III) and worked up as usual to yield 2.46 g (80%) of XV, mp 110–113° dec, ir bands at 5.55, 5.76, and 6.02; nmr bands at 3.41 (singlet, 3 H, O-CH$_3$), 4.25 (singlet, 2 H, CH$_2$).

Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.5; H, 4.7. Found: C, 68.5; H, 4.6.

The same compound was obtained in similar yield on stirring the sodium salt of III with methyl chlorocarbonate in ether at room temperature for 4–6 hr.

When XV was heated in refluxing benzene for 2 hr, it was recovered unchanged in high yield. However, on heating neat at 110–115° for 2 hr carbon dioxide was evolved (approximately quantitative), and 3-phenylisocoumarin (XVI),[7,12] mp 89–90°, was obtained in 95% yield. Treatment of III with thionyl chloride also yielded XVI in high yield.

1-Ethoxyvinyl *o*-**Phenacylbenzoate** (XVII). To a stirred solution at −40 to −50° of 1.4 g of ethoxyacetylene[26] and 0.1 g of mercuric acetate in 25 ml of dry methylene chloride was added a solution of 2.4 g of III in 5 ml of CH$_2$Cl$_2$ during 1 hr. The cooling bath was removed and when room temperature was reached the usual work-up (solvent removed in the cold) afforded an oily residue which crystallized to yield XVII (90%), mp 81–83°, ir bands at 5.75, 5.96, and 6.03; nmr bands at 1.2 (triplet, 3 H, CH$_3$), 3.6 (singlet, 2 H, ═CH$_2$), 3.67 (quartet, 2 H, O*CH*$_2$CH$_3$), 7.4–7.9 (9 H, aromatic).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.5; H, 5.8. Found: C, 73.3; H, 5.7.

Alkaline hydrolysis of XVII afforded III in quantitative yield.

On heating 1.0 g of XVII at 140° for 2 hr ethyl acetate was evolved (identified by glpc analysis) and XVI, mp 89-90°, was obtained in very high yield. Heating experiments at lower temperatures (as low as 110°) also yielded similar results except that longer periods of heating were required.

Anhydride (*n-n*) **of** *o*-**Phenacylbenzoic Acid.** A solution of 0.36 g of ethoxyacetylene in 10 ml of CH$_2$Cl$_2$ was added during 15 min to a solution of 2.4 g of III and 0.1 g of mercuric acetate in 75 ml of CH$_2$Cl$_2$ at −70°. After 1 hr at −70° and 2 hr at room temperature the mixture was worked up as usual to yield 1.71 g (75%) of the anhydride, mp 147-149°; nmr bands at 4.1 (singlet, 2 H, CH$_2$CO) and 7.4–7.7 (multiplet, 9 H, aromatic H).

Anal. Calcd for $C_{30}H_{22}O_5$: C, 77.9; H, 4.8. Found: C, 78.3; H, 5.0.

Mixed Anhydride of *o*-**Benzoylphenylacetic and Methylcarbonic Acids** (XX). When a mixture of IV and methyl chlorocarbonate was treated as described for XII, a red oil was obtained which resisted efforts at crystallization. That this oil was essentially pure XX was indicated by the nmr, 3.84 (singlet, 2 H, CH$_2$) and 3.42 (singlet, 3 H, OCH$_3$).

When this oil was heated at 100-110°, carbon dioxide was evolved (quantitatively) and a darker red oil (XXI) was obtained which was obviously polymeric. When maleic anhydride or vinylene carbonate[13] were added prior to the heating, the product was essentially the same. No trace of adduct was isolated. A similar red polymeric oil was produced when IV was heated with thionyl chloride.[6]

1-Ethoxyvinyl *o*-**Benzoylphenylacetate** (XXII). To a solution at −70° of 1.4 g of ethoxyacetylene in 25 ml of CH$_2$Cl$_2$ containing 0.1 g of mercuric acetate was added a solution of 2.4 g of IV in 125 ml of CH$_2$Cl$_2$ during 30 min. After stirring for 1 hr at room temperature the CH$_2$Cl$_2$ was removed under vacuum and the residue was worked up as usual. The temperature during work-up was always room temperature or below. All attempts at low-temperature crystallization or column chromatography failed to yield a crystalline product. However, spectral analysis supported XXII as the structure: nmr bands at 1.18 (triplet, 3 H, CH$_3$), 3.58 (quartet, 2 H, OCH$_2$), 3.52 (singlet, 2 H, C═CH$_2$), 3.81 (singlet, 2 H, C$_6$H$_5$-CH$_2$), 7.3–7.7 (multiplet, 9 H, aromatic–H).

When XXII was heated in the 120–140° range ethyl acetate was evolved and a red oily polymer similar to that described above was obtained.

---

(23) For rationalization of the uv data, see ref 3a, Table I, and the discussion concerning anhydride structures.

(24) O. Grummitt, R. Egan, and A. Buck, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 449.

(25) A compound stated to be methyl *o*-phenacylbenzoate, mp 88–89°, was reported by M. Renson and L. Christiaens, *Bull. Soc. Chim. Belges*, 71, 443 (1962). However, no analysis was given.

(26) Obtained from the Chemicals Samples Co., Columbus, Ohio.