were replaced each 2 hr. The chloride ion formed was estimated by volumetric titration with mercuric nitrate.[8]

Analysis of Products.—All nongaseous products were detected by gas chromatography, using a 1/4-in. column packed with 5% FFAP on Chromosorb W, and compared with authentic samples.

Registry No.—Propionic acid, 79-09-4; butyric acid, 107-92-6; valeric acid, 109-52-4; N,N-dimethylacetamide, 127-19-5; N,N-dimethylpropionamide, 758-96-3; N,N-dimethyllbutyramide, 760-79-2.

(8) "Standard Methods for the Examination of Water and Waterwaste," 12th ed, American Public Health Association, New York, N. Y., 1965, p 87.

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Steric Effects in Intramolecular Rearrangements Involving a [3.2.1]-Bicyclic Mechanism[1]

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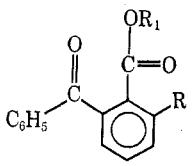
Pyrolyses of 1-ethoxyvinyl 2-benzoylbenzoate (**5**), 1-ethoxyvinyl 6-methyl-2-benzoylbenzoate (**6**), 1-ethoxyvinyl 3-methyl-2-benzoylbenzoate (**7**), and 1-ethoxyvinyl 3,6-dimethyl-2-benzoylbenzoate (**8**) have been studied. Qualitative studies show that the methyl group in the 6 position facilitates the rearrangement to lactone ester whereas a methyl group in the 3 position hinders the rearrangement. An explanation for the facts is presented.

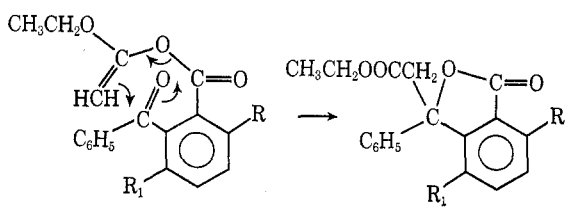
The idea that bicyclic mechanisms might be involved in organic reactions arose from the facts that the rate of alkaline hydrolysis of methyl 6-methyl-2-benzoylbenzoate (**1**) is greater than that of methyl 2-benzoylbenzoate[2] (**2**) and the rate of acid-catalyzed esterification of 6-methyl-2-benzoylbenzoic acid (**3**) is greater than that of 2-benzoylbenzoic acid[3] (**4**). These facts were explained by assuming that attack of the reagent in question took place mainly at the ketonic group rather than at the carbonyl group of the carboxyl function.



1, R = CH_3; R_1 = CH_3
2, R = H; R_1 = CH_3
3, R = CH_3; R_1 = H
4, R = H; R_1 = H

By synthesizing compounds which had functions at R_1 which could lead to intramolecular cyclization, reactions were found to occur on pyrolysis in which groups ended up preferentially on the ketonic carbonyl carbon rather than the carboxylic carbon. The mechanisms by which these reactions occur have been termed bicyclic mechanisms.[4]

In previous work, no study of steric effects on the rate of reactions proceeding by bicyclic mechanisms was made. In this paper the relative rate of thermal rearrangement of ethoxyvinyl 2-benzoylbenzoate (**5**), ethoxyvinyl 6-methyl-2-benzoylbenzoate (**6**), and ethoxyvinyl 3,6-dimethyl-2-benzoylbenzoate (**8**) to the corresponding lactone esters 5_{LE}, 6_{LE}, and 8_{LE} have



5, R = R_1 = H
6, R = CH_3; R_1 = H
7, R = H; R_1 = CH_3
8, R = R_1 = CH_3

5_{LE}
6_{LE}
7_{LE}
8_{LE}

been determined qualitatively. As the rate of rearrangement of **6** was greater than that for **5**, **7**, and **8**, the steric assistance noted in alkaline hydrolysis[2] and acidic esterification[3] is also of importance in the intramolecular [3.2.1]-bicyclic rearrangement. However, the presence of a methyl group in the 3 position in compounds **7** and **8** retards the bicyclic path strongly. In the case of **7** rearrangement to 7_{LE} did not occur. Instead, at the temperature of 200–220° needed for pyrolysis, only the normal-pseudo anhydride of 3-methyl-2-benzoylbenzoic acid was formed. Since pyrolysis of **8** gives mainly 8_{LE}, another example of the favorable effect of a methyl group in the 6 position is provided as it overcomes the unfavorable effect of the methyl group at the 3 position.

The favorable effect of the 6-methyl group in the rearrangements of **6** and **8** relative to **5** and **7**, respectively, is probably due to two factors: (a) the steric effect of the 6-methyl group which keeps the carboxyl function from coplanarity with the ring (raising the energy of the ground state for the rearrangement) and (b) the relief of strain in the product (lowering the energy of the transition state). The adverse effect of the 3-methyl group probably acts mainly by increasing

(1) This research was supported in part by Grant 5552 of The National Science Foundation and by Grant DA-ARO-D-31-124-G846 from the U. S. Army Research Office, Durham, N. C.

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

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

(4) A bicyclic mechanism is defined as an intramolecular cyclic mechanism in which the atoms involved in change of bonding are not in a continuous chain. In cyclic mechanisms the atoms involved form a continuous chain. For examples of [3.2.1]-, [3.3.1]-, and [4.2.2]-bicyclic mechanisms, see the following articles and references therein: (a) M. S. Newman and C. Courduvelis, *J. Amer. Chem. Soc.*, **88**, 781 (1966); (b) M. S. Newman, S. Mladenovic, and L. K. Lala, *ibid.*, **90**, 747 (1968).

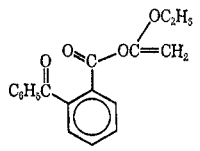
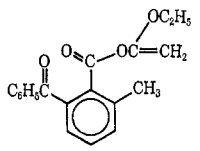
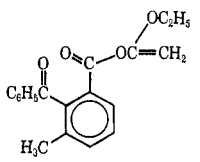
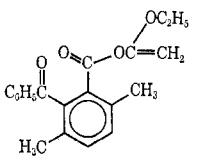
the energy of the transition state due to conventional steric hindrance to addition to a carbonyl group.

The requisite 2-benzoylbenzoic acids were prepared by known methods (see Experimental Section). The mixture of 6-methyl-2-benzoylbenzoic acid (6_A) and 3-methyl-2-benzoylbenzoic acid (7_A) obtained by the Friedel–Crafts condensation of 3-methylphthalic anhydride with benzene[5] was separated in part into the two pure acids by fractional recrystallization. By heating a mixture of 6_A and 7_A in 100% sulfuric acid solution at 70° the mixture was converted in high yield to almost pure 6_A.[6]

The ethoxyvinyl esters, **5–8**, prepared as described,[4a,7] were heated neat in carefully cleaned flasks to give the results listed in Table I. Previously, thermal rearrangement of the mixed anhydride of methyl carbonic and *o*-benzoylbenzoic acids was shown to occur unimolecularly.[8] We assume that the analogous thermal rearrangement of the ethoxyvinyl esters is also unimolecular.

TABLE I

PYROLYSES OF ETHOXYVINYL ESTERS

Compd		Temp, °C[a]	Lactone-ester[b]	Anhydride[c]
5		180	>90	None
6		150	80	10
7		200[d]		>90
8		200	85	8[e]

[a] Temperature needed for 1 hr of pyrolysis to cause a minimum of 95% disappearance of starting vinyl ester. [b] Per cent isolated as lactone–ester. [c] Isolated yields of n,ψ-anhydrides.[4a] [d] Pyrolysis of **7** for 2 hr yielded only the n,ψ-anhydride. [e] The structure of this anhydride is uncertain (see Experimental Section).

The rearrangements of **5** and **7** to 5_{LE} and 7_{LE} was markedly catalyzed by boron fluoride etherate. Presumably these acid-catalyzed rearrangements also occur by a [3.3.1]-bicyclic mechanism. Additional examples of boron fluoride catalyzed bicyclic rearrangements are to be presented in the near future.

Interestingly the α hydrogens of the acetic ester grouping in 6_{LE} (and of the corresponding acetic acid grouping) appear as a singlet on the 60-Mc instrument whereas the corresponding methylene hydrogens in 7_{LE} and 8_{LE} appear as an AB quartet.

Experimental Section[9]

3-Carbethoxymethyl-3-phenylphthalide (5_{LE}).—Pure 1-ethoxyvinyl 2-benzoylbenzoate (**5**), mp 74–75°, prepared as described[4a] and recrystallized from benzene–hexane, was obtained in 92% yield. On pyrolysis at 200° for 30 min 5_{LE} was produced exclusively. Crystallization from benzene–hexane yielded colorless crystals, mp 95–96°, in over 90% yield.

On allowing a solution of 2.0 g of **5** in 50 ml of methylene chloride containing a few drops of boron trifluoride etherate to stand for 12 hr at room temperature pure 5_{LE} was produced in 85% yield.[10]

1-Ethoxyvinyl 6-Methyl-2-benzoylbenzoate (**6**).—The preparations of the ethoxyvinyl esters were carried out as described.[4a] Using 6-methyl-2-benzoylbenzoic acid[5] yields of 61–81% pure **6** were obtained: mp 75.0–75.5°; nmr 8.75 (t, 3 H, J = 7.5 Hz, OCH_2CH_3), 7.47 (s, 3 H, $ArCH_3$), 6.55–6.00 (m, 4 H, OCH_2CH_3, $OC{=}CH_2$ the dd of $OC{=}CH_2$ is not distinguishable from the quartet of OCH_2CH_3), 2.85–2.12 (m, 8 H, ArH).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.5; H, 5.9. Found: C, 73.2; H, 5.7.

3-Carbethoxymethyl-7-methyl-3-phenylphthalide (6_{LE}).—On pyrolysis of 1.0 g of **6** at 160° for 1 hr and trituration of the cooled mixture with ether, there was obtained 0.15 g of a solid, mp 184–186°, and an oily remainder. Recrystallization from benzene–ligroin yielded the pure n,ψ-anhydride: mp 186–187°; nmr 7.63 (s, 3 H, $ArCH_3$), 7.46 (s, 3 H, $ArCH_3$), 2.88–2.28 (m, 16 H, ArH). The different methyl signals rule out n,n- and ψ,ψ-anhydrides.

Anal. Calcd for $C_{30}H_{22}O_5$: C, 77.7; H, 4.8. Found: C, 77.7, 77.9; H, 4.8, 5.1.

Bulb-to-bulb distillation of the oil [air bath at 170–175° (0.002 mm)] yielded 0.8 g (80%) of an oil. Redistillation with little loss afforded oily 6_{LE}: nmr 9.01 (t, 3 H, J = 7.5 Hz, OCH_2CH_3), 7.30 (s, 3 H, $ArCH_3$), 6.60 (s, H, CH_2CO), 6.10 (q, 2 H, J = 7.5 Hz, OCH_2CH_3), 2.90–2.33 (m, 8 H, ArH).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.5; H, 5.9. Found: C, 73.5; H, 6.2.

Alkaline hydrolysis yielded 3-carboxymethyl-7-methyl-3-phenylphthalide: mp 169–170°; nmr (acetone-d_6), 7.31 (s, 3 H, $ArCH_3$), 6.40 (s, 2 H, CH_2CO), 2.68–2.32 (m, 8 H, ArH), 2.30 (s, 1 H disappears on adding D_2O, COOH), in high yield.

Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0. Found: C, 72.1; H, 4.8.

1-Ethoxyvinyl 3-Methyl-2-benzoylbenzoate (**7**).—By treatment of 4.8 g of 3-methyl-2-benzoylbenzoic acid[5] with ethoxyacetylene[4a] there was obtained 5.9 g (95%) of colorless **7**, mp 98–101°. Recrystallization from benzene–hexane with little loss yielded **7**: mp 101–102°; nmr 8.83 (t, 3 H, J = 7.5 Hz, OCH_2CH_3), 7.89 (s, 3 H, $ArCH_3$), 6.57–6.13 (m, 4 H, OCH_2CH_3, $OC{=}CH_2$, the dd of $OC{=}CH_2$ is not distinguishable from the quartet of OCH_2CH_3), 3.00–2.18 (m, 8 H, ArH).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.5; H, 5.8. Found: C, 73.7; H, 5.6.

After treatment of 1.8 g of **7** in methylene chloride with boron trifluoride ethereate as described above[9] for **5**, the methylene chloride was removed on a rotary evaporator. By crystallization of the residue from benzene–hexane there was isolated 0.6 g (45%) of the n,ψ-anhydride, mp 165–168°. A recrystallized sample melted at 168–169°; nmr 8.08 (s, 3 H, $ArCH_3$), 7.92 (s, 3 H, $ArCH_3$), 2.78–2.28 (m, 16 H, ArH). On alkaline hydrolysis 3-methyl-2-benzoylbenzoic acid[5] was obtained.

Anal. Calcd for $C_{30}H_{22}O_5$: C, 77.7; H, 4.8. Found: C, 77.5; H, 4.8.

On bulb-to-bulb distillation [bath temperature 165–170° (0.001 mm)] there was obtained 0.43 g (24%) of **7** as a pale yellow oil: nmr 9.10 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 7.83 (s, 3 H,

(5) M. S. Newman and C. D. McCleary, *J. Amer. Chem. Soc.*, **63**, 1542 (1941).

(6) For an explanation, see M. S. Newman and K. G. Ihrman, *ibid.*, **80**, 3652 (1958).

(7) H. H. Wasserman and P. S. Wharton, *ibid.*, **82**, 661 (1960).

(8) M. S. Newman and L. K. Lala, *J. Org. Chem.*, **32**, 3225 (1967).

(9) All melting points and boiling points are uncorrected. Analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn. All flasks used for pyrolysis experiments were steamed for 30 min and dried before use. The ethoxyacetylene used (Farchan Laboratories, Willoughby, Ohio) was redistilled and stored in ampoules in the cold chamber of a refrigerator until used. When pure, ethoxyacetylene can be stored thus for long periods. Nmr spectra were taken in $CDCl_3$ and are expressed in τ relative to $(CH_3)_4Si$, 10.0.

(10) D. Cohen and G. E. Pattenden, *J. Chem. Soc. C*, 2314 (1967).

$ArCH_3$), 6.40–5.92 (m, 4 H, CH_2CO, OCH_3CH_3, the dd of CH_2CO is not distinguishable from the quartet of OCH_2CH_3), 2.78–2.10 (m, 8 H, ArH).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.5; H, 5.8. Found: C, 73.9; H, 5.9.

On pyrolysis of 0.80 g of **7** at 200° for 2 hr there was obtained 0.6 g (97%) of n,ψ-anhydride, mp and mmp (with above anhydride) 168–169°.

1-Ethoxyvinyl 3,6-Dimethyl-2-benzoylbenzoate (8).—Treatment of 3,6-dimethyl-2-benzoylbenzoic acid[11] as described[4a] yielded **8**, mp 73–75° in almost quantitative yield. Recrystallization from ether–petroleum ether (bp 30–60°) gave with little loss colorless **8**: mp 74.5–75.5°; nmr 8.77 (t, 3 H, J = 7.5 Hz, OCH_2CH_3), 7.89, 7.49 (each s, 3 H, $ArCH_3$), 6.53 (dd, 2 H, J = 3.5 Hz, $=CH_2$), 6.30 (q, 2 H, J = 7.5 Hz, OCH_2CH_3), 2.88–2.10 (m, 7 H, ArH).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2. Found: C, 73.9; H, 6.2.

3-Carboethoxymethyl-4,7-dimethyl-3-phenylphthalide (8_{LE}).—Pyrolysis of 4.68 g of **8** at 220–230° for 1 hr yielded a mixture which on trituration afforded 0.55 (8%) of solid, mp 255–260°. After two recrystallizations from benzene–petroleum ether a solid, mp 278–280°, was obtained with little loss. Because of limited solubility no nmr was run. We are uncertain of the structure of this anhydride.

Anal. Calcd for $C_{32}H_{26}O_5$: C, 78.3; H, 5.3. Found: C, 78.6; H, 5.7.

Bulb-to-bulb distillation of the remainder of the pyrolysis products (0.05 mm) yielded a liquid which was redistilled to yield 4.1 g (85%) of 8_{LE} as a pale yellow oil which distilled (two-bulb system) with the heating bath at 185–190° (0.0014 mm); nmr 9.05 (t, 3 H, J = 7.0 Hz, OCH_2CH_3), 7.88, 7.30 (each s, 3 H, $ArCH_3$), 6.38 (dd, 2 H, J = 14.8 Hz, CH_2CO), 6.11 (q, 2 H, J = 7.0 Hz, OCH_2CH_3), 2.70 (each s, 7 H, ArH).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2. Found: C, 73.9; H, 6.3.

3-Carboxymethyl-4,7-dimethyl-3-phenylphthalide.—On hydrolysis with barium hydroxide, 2.0 g of 8_{LE} yielded 1.4 g (89%) of colorless needles (from chloroform–benzene) of acid: mp 155.0–155.5°; nmr (acetone-d_6), 7.84, 7.31 (each s, 3 H each, $ArCH_3$), 6.24 (dd, J = 15.0 Hz, CH_2CO), 2.63 (s, 1 H, disappears on addition of D_2O, COOH), 2.58 (s, 7 H, ArH).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4. Found: C, 73.0; H, 5.5.

Pyrolysis Experiments, Table I.—The esters **5–8** were heated in flasks which had been steamed out for 30 min and dried. Disappearance of nmr bands in the τ 6.33–6.48 region (characteristic of the vinyl hydrogens) was taken as a measure of completion of reaction.

Registry No.—**5**, 6158-56-1; 5_{LE}, 6158-57-2; **6**, 24766-40-3; **6** anhydride, 24766-41-4; 6_{LE}, 24766-42-5; **7**, 24766-43-6; **7** anhydride, 24766-44-7; **8**, 24766-45-8; 8_{LE}, 24766-46-9; 3-carboxymethyl-7-methyl-3-phenylphthalide, 24766-47-0; 3-carboxymethyl-4,7-dimethyl-3-phenylphthalide, 24766-48-1.

(11) M. S. Newman and B. T. Lord, *J. Amer. Chem. Soc.* **66**, 733 (1944).

The Acid-Catalyzed Nitramine Rearrangement. VII. Intramolecularity[1-3]

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Concurrent rearrangement of N-nitro-N-methylaniline and *p*-fluoro-N-nitro(^{15}N)-N-methylaniline yielded *p*-nitro-N-methylaniline containing a considerable excess of ^{15}N. This indication of intermolecularity in the nitramine rearrangement was strengthened by the exclusion of other possible pathways for the formation of *p*-nitro(^{15}N)-N-methylaniline. It was found that the yields of nitroanilines were reduced and the nitro-group exchange was eliminated in the presence of reducing agents, suggesting that they intercept the species involved in the intermolecular process. These results are readily interpreted in terms of a previously proposed mechanism.

Most mechanisms for the nitramine rearrangement are based upon the need to account for the intramolecularity of the reaction. A varied series of studies support the assumption of intramolecularity. Rearrangement of N-nitroaniline in 85% sulfuric acid at 10° yielded only *o*- and *p*-nitroanilines while nitration of aniline under similar conditions gave chiefly the *meta* and *para* isomers.[4,5] If the nitramine dissociated into aniline and nitronium ion during the rearrangement, then the product should have been identical to that from direct nitration.

A number of investigators have shown that a nitro group is not transferred from rearranging nitramine to an easily nitratable substance added to the reaction medium. Thus, the acid-catalyzed rearrangement of 2,4,6-tribromo-N-nitroaniline in the presence of either acetanilide or 2,4-dichloroaniline failed to produce nitroacetanilide or 2,4-dichloro-6-nitroaniline.[6] Similarly, it was found that when N,4-dinitro-N-methylaniline was converted to 2,4-dinitro-N-methylaniline in the presence of xylene or phenol, no nitroxylenes or nitrophenols were formed and no *p*-nitro-N-methylaniline (from loss of a nitro group) could be detected. Thus, no substance that could nitrate acetanilide, 2,4-dichloroaniline, *p*-xylene, or phenol existed during these rearrangements. However, the behavior of N,2,4-trinitro-N-methylaniline[5] is somewhat paradoxical. In 80% sulfuric acid, this compound yielded the expected product, 2,4,6-trinitro-N-methylaniline, but in other acid media, such as dilute hydrochloric acid and acetic–sulfuric acid mixtures, the denitration product, 2,4-dinitro-N-methylaniline, was obtained. Furthermore, when the rearrangement was conducted in sulfuric acid in the presence of *p*-xylene, 2-nitro-1,4-xylene and 2,4-dinitro-N-methylaniline were isolated

(1) Previous papers in this series: (a) W. N. White, D. Lazdins, and H. S. White, *J. Amer. Chem. Soc.*, **86**, 1517 (1964); (b) W. N. White, C. Hathaway, and D. Huston, *J. Org. Chem.*, **35**, 737 (1970); (c) W. N. White and J. R. Klink, *ibid.*, **35**, 965 (1970); (d) W. N. White, J. T. Golden, and D. Lazdins, *ibid.*, **35**, 2048 (1970); (e) W. N. White and H. S. White, *ibid.*, **35**, 1803 (1970).

(2) Part of this work has been reported in a preliminary form: W. N. White, J. R. Klink, D. Lazdins, C. Hathaway, J. T. Golden, and H. S. White, *J. Amer. Chem. Soc.*, **83**, 2024 (1961).

(3) This work was supported by Grants G-7345 and GP-1970 from the National Science Foundation.

(4) A. F. Holleman, J. C. Hartogs, and T. van der Linden, *Ber.*, **44**, 704 (1911).

(5) E. D. Hughes and G. T. Jones, *J. Chem. Soc.*, 2678 (1950).

(6) K. J. P. Orton, *Chem. News*, **106**, 236 (1912).