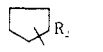
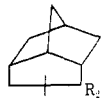
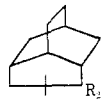
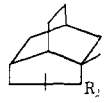
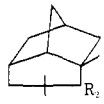
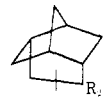
Table I. Steric Effects on Lactonization as Computed from Hydrocarbon Models

Compound[a]	$-\Delta\Delta V_s^b/1.4$ R = H	$-\Delta\Delta V_s^b/1.4$ R = CH_3	log k_{rel}[c]
A 	0	0	0
B 	3.4 (4.4)	2.6 (3.6)	4.11
C 	−0.2 (0.3)	0 (0.5)	1.04
D 	2.9 (2.9)	2.5 (2.5)	1.92
E 	3.6 (4.1)	3.0 (3.5)	4.1
F 	6.7 (7.7)	3.7 (4.7)	*d*
G 	−1.7 (−0.2)	−6.4 (−4.9)	*d*

[a] Line across bond designates position of formal ring closure. For compound B, for example, see eq 1–3. [b] (V_s for **2**, $-V_s$ for **1**) − (ΔV_s for cyclopentane for 1,1-dimethylcyclopentane). The 1.4 factor is $2.3RT$ for 25°. The values in parentheses include a $T\Delta S$ correction. See text. [c] Reference 2. [d] See ref 3.

ergies V_s by means of molecular mechanics.[4-8] The strain energy, eq 4, is defined in terms of deviations of

$$V_s = \frac{1}{2}k_{ij}(p_{ij} - p_{ij}^0)^2 + V_{nb}(r_{kl}) + \text{other terms} \quad (4)$$

bond lengths and angles, p_{ij}, from reference values, p_{ij}^0, assuming a Hooke's law function, plus terms which evaluate pairwise nonbonded energies plus other terms which evaluate Pitzer strain and certain corrections. We have used the Allinger[7] force field as described except for dividing torsional effects into nine parts to ensure consistency.[9] Results are presented in Table I.

Although the calculation is made for a static model, the method is parameterized to reflect enthalpies due to steric effects for hydrocarbons in the vapor phase at 298°K. It appears that the reliability of the double differences $\Delta\Delta V_s$ may be of the order of 2–3 kcal/mol at the present state of development. Values have been related to γ-butyrolactone and its models taken as 0. If the model is successful, the values in columns 2 and 3 of Table I should reproduce those of column 4. The agreement is as good as can be expected for the calculated steric energies. We conclude that the approach is a useful one for predicting relatively large steric effects.

Several comments are in order. Computations based directly on the oxygen compounds **1** and **2** will certainly be in order as force fields for these compounds become more fully developed, but it will require considerable evaluation to determine whether these are more reliable than improved hydrocarbon calculations or on modifications based on hydrocarbon models. Perhaps of more importance will be evaluation of entropy changes, which can be obtained from molecular mechanics.[6,10] We have approximated the entropy ($T\Delta S$) terms by the estimated ΔG values in parentheses. These were based on an evaluation of the entropy changes in forming various ring compounds taken from thermodynamic data on hydrocarbons.[11] Cyclopentane has a relatively high entropy in comparison with *n*-pentane, while 2,6-dimethylbicyclo[2.2.1]heptane is relatively constrained in comparison with the tricyclo compound (B in Table I), and this is estimated to give a $T\Delta S$ term of about 1.5 kcal/mol (or 1 in log k_{rel}).

Care is needed in using CH_3 groups to represent oxygen atoms, for the extra hydrogen atoms may encounter steric compressions not expected for an -OR group. We therefore examined the nonbonded distances carefully for such artifacts. These are minimal for compounds A–E but are of some consequence in F. It is easy to modify hydrocarbon models to remove such artifacts should this prove advantageous.

Acknowledgment. It is a pleasure to acknowledge the inspiration of the work of Professor L. S. Bartell and his generosity in supplying his program for molecular mechanics computations. It is also a pleasure to acknowledge the hospitality of Professor J. Dunitz at the Eidgenossiche Technische Hochschule, Zurich, which permitted me to undertake development of an expanded molecular mechanics program. Dr. Hans Buergi of ETH was a most helpful guide. This work was supported in part by Contract No. AF(40-1)-2690 under the Division of Biology and Medicine, U. S. Atomic Energy Commission. I am also indebted to the Computing Center at Florida State University for a grant of computer time.

(4) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 523.
(5) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47**, 3736 (1967); L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).
(6) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).
(7) M. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).
(8) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).
(9) Allinger's convention uses torsion angles of 60° or less. In certain compounds this convention omits one torsion term or adds an extra. In most cases the two conventions give results which agree within about 0.5 kcal/mol or better.
(10) K. B. Wiberg and R. H. Boyd, *J. Amer. Chem. Soc.*, **94**, 8426 (1972).
(11) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

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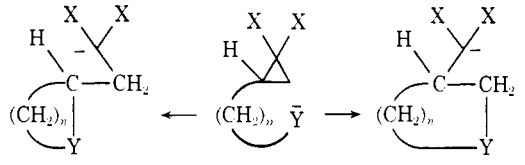
Ring Construction through Transpositions of Activated Cyclopropanes

Sir:

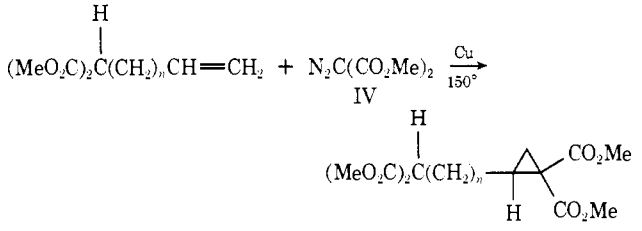
Recently, we reported an instance of homoconjugate addition by a nucleophile disposed to execute intra-

molecular opening of an activated cyclopropane.[1] In the general case, two variations of attack may be envisioned. To emphasize the transition-state relationship of the ring in the process of formation, with the cyclopropane suffering disconnection, we term these the spiro and fused modes. It has been our contention that the mutation of cyclopropanes[2-5] into thermodynamically more stable rings poses an attractive possibility for the assembly of otherwise less accessible systems. Crucial to the realistic application of this concept is some predictive capacity relevant to the question of the spiro *vs.* fused modes. Below we report the outcome of experiments addressed to this issue. These results are indicative of the wide potentialities of the method.



spiro mode fused mode

The substrates employed in this study were tetraesters I, II, and III. These compounds were each prepared *via* the copper catalyzed reaction of the precursor olefinic malonates with dimethyl diazomalonate (IV).[6] In the typical case, a solution of 1 equiv of olefin and 1 equiv of IV was added dropwise to a mixture of 1 equiv of neat olefin and copper metal (0.5 g of copper per 0.1 mol of IV) maintained at 150°. In each case, the products were purified by chromatography on silica gel. These preparations are summarized below.

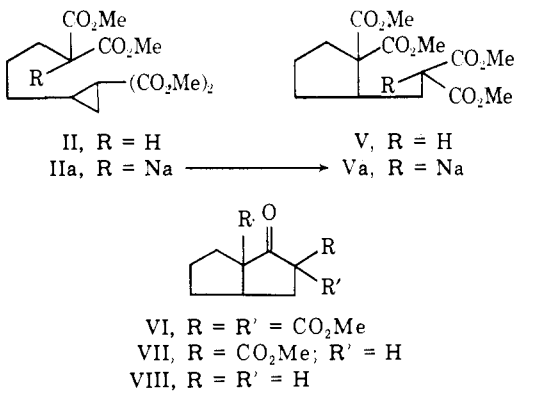


Starting material	Product	Yield (%)
$n = 2$	I	71
$n = 3$	II	84
$n = 4$	III	83

Solutions of the anions, Ia, IIa, and IIIa were prepared by treating the tetraesters with 1.1 equiv of dimsyl sodium–DMSO.[7] We report first the similar and relatively simple chemistry of anions IIa and IIIa and then the more complex behavior exhibited by Ia.

After 3 hr at room temperature, followed by neutralization, IIa was transformed in 84% to V.[8] No other isomeric products were detected under these conditions. The half-life for the isomerization of IIa → Va at room temperature is 25 min. In a separate experiment, after the reaction was conducted at room temperature under the aforedescribed conditions, the temperature was raised to 90–93° for 24 hr. After quenching and chromatography on silica gel, a 71% yield of 2,7-dicarbomethoxybicyclo[3.3.0]octan-1-one (VII)[8] was obtained. This product presumably arises from decarbomethoxylation of VI, the Dieckmann product of Va. The propensity for cyclization–decarbomethoxylation of bis malonates (Va and IXa) in DMSO was an unexpected though welcome feature of the reaction sequence.

Hydrolysis of VII (concentrated HCl–EtOH, 120°) is accompanied by decarboxylation, thereby affording the known *cis*-bicyclo[3.3.0]octan-1-one (VIII) isolated in 77% yield as its semicarbazone derivative, mp 177–178° (lit.[9] 178–180°). This simple entry to the hydropentalane series is summarized below.



A solution of IIIa in DMSO was stable at room temperature for extended periods of time. However, at 80° after 5 hr, two new products, IX[8] (43%) and XI[7] (16%), were detected in addition to unreacted III.[10] The former was purified by glpc on a 12 ft × 1/2 in. 3% SE-30 column isothermally at 200°. When the reaction was conducted at 94–95° for 24 hr a 72% isolated yield of XI was obtained. Compounds III and IX were no longer detected after these conditions. Again, it seems reasonable to suppose the XI arose from X by decarbomethoxylation. Exhaustive (20% HCl–70% H_2O–10% EtOH) hydrolysis and decarboxylation of XI gives the epimeric perhydroindan-1-one mixture (XII) characterized through its semicarbazone derivative, mp 204–208° (lit.[11] 212° for a 10:1 cis:trans mixture).

The cis junction stereochemistry indicated for XI was

(1) S. Danishefsky, J. Dynak, and M. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 81 (1973).

(2) An unsuccessful attempt to realize intramolecular homoconjugate addition is seen in the work of Maercker. See A. Maercker and W. Theyson, *Justus Liebigs Ann. Chem.*, **759**, 132 (1972). The absence of reaction in those cases may be a consequence of insufficient activation of the cyclopropane. Also, the Grignard-type reagents in ether solvents may be substantially less reactive than the sodium enolates in DMSO employed in this study.

(3) Conceptually related and successful analogs of this process are seen in the studies of Stork and coworkers wherein the electrophile is a cyclopropyl ketone attacked by Lewis acid and the nucleophile is either a proximate aryl[4a] or olefinic[4b] system. The stereospecificity manifested by epimeric substrates suggests that these reactions indeed correspond to nucleophilic attack on the cyclopropane. It is interesting to note that they involve the fused rather than the spiro mode observed here.

(4) (a) G. Stork and M. Gregson, *J. Amer. Chem. Soc.*, **91**, 2373 (1969); (b) G. Stork and P. A. Grieco, *ibid.*, **91**, 2407 (1969).

(5) For intramolecular opening of epoxides see (a) H. Smith, P. Wegfahrt, and H. Rapoport, *J. Amer. Chem. Soc.*, **90**, 1668 (1968); (b) G. Stork, Abstracts, 23rd National Organic Symposium of the American Chemical Society, Division of Organic Chemistry, Tallahassee, Fla., June 1973.

(6) *Cf.* B. W. Peace and D. S. Wulfman, *Synthesis*, 137 (1973). Tetracarbomethoxyethane is the major by-product. See E. Ciganek, *J. Org. Chem.*, **30**, 4366 (1965).

(7) E. J. Corey and Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

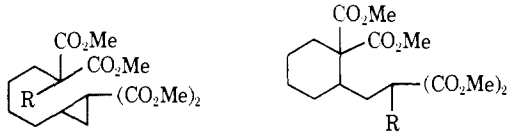
(8) The structure of this compound is in accord with (a) its infrared, nmr, and mass spectra and (b) its combustion analysis.

(9) A. C. Cope and W. R. Schmitz, *J. Amer. Chem. Soc.*, **72**, 3056 (1950).

(10) Yields were obtained by quantitative glc on a 6 ft × 1/8 in., 3% SE-30 column 80° programmed at 10°/min, flow rate 25 ml/min. Under these conditions, compound XI is converted to XIII either on the column or in the injection port. The retention times are: XIII (from XI), 4.3 min; IX, 11.5 min; VIII, 12.5 min.

(11) D. W. Mathieson, *J. Chem. Soc.*, 3248 (1953).

established as follows. Selective hydrolysis–decarboxylation (1% HCl; 4:1 EtOH–H_2O; reflux 48 hr) affords XIII[8a] (semicarbazone mp 199–201°) which was converted ((i) 1,2-ethanedithiol–BF_3–dioxane; (ii) Raney nickel–ethanol; (iii) KOH–ethanol) without purification of intermediates into acid XIV,[8a] mp 40–43°, identical with an authentic sample prepared *via* hydrogenation of the Diels–Alder adduct of cyclopentene-1-carboxylic acid with 1,3-butadiene.[12] The new entry to the angularly functionalized *cis*-hydrindan series is summarized below.



III, R = H
IIIa, R = Na ⟶ IXa, R = Na
IX, R = H

X, R = R′ = CO_2Me
XI, R = CO_2Me, R′ = H
XII, R = R′ = H
XIII, R = Me; X = O
XIV, R = H; X = H_2

In both cases described above, the new ring is produced exclusively in the spiro mode and is stable to the reaction conditions. A more complicated instance of ring transpositions was encountered in the reactions of Ia. The cyclization options (four-membered ring *via* the spiro mode, five-membered ring *via* the fused mode) available to this substrate were of particular interest in determining any intrinsic preference for the spiro pathway. Such a preference could not be inferred from our previous study[1] or from the isomerizations of IIa and IIIa since cyclizations leading to three-,[1] five-, and six-membered rings in preference to four-, six-, and seven-membered rings, respectively, are in accord with more general precedents governing the relative propensity for ring-forming reactions.[13]

Heating a solution of Ia in DMSO at 110° for 5 hr afforded, after neutralization and chromatography, a 44% yield of XV.[8] Two minor products, XVII[7a] (Dieckmann product[14] of XVa) and XVIII[7a] (decarbomethoxylation product of XVII), were each isolated in 4% yield. Their structures were confirmed by their conversion (HCl–H_2O–EtOH; reflux 48 hr) to β-keto-acid XIX, mp 125.5–128°, lit.[15] 128–129°.

In addition to XV and recovered I, traces of another isomer *m/e* 316 were detected by analysis of the crude reaction mixture *via* combined glc–mass spectrometry. When, in separate runs, the progress of the reaction was monitored by examination of aliquots by glc,[16] a buildup of this isomer followed by its subsequent diminution in favor of XV was noted. For instance, after 10 min this isomer was present in a ratio of 15:77:8 relative to I and XV. The optimum buildup of this isomer arises after *ca.* 30 min when it is present in a ratio of 21:52:27 relative to I:XV. After this interval, the material was obtained in pure form by preparative[16] glc and identified as XVI.[8]

Treatment of XVI with 1.1 equiv of dimsylsodium–DMSO at 110° for 24 hr gave a 47% (isolated) yield of XV. When the progress of this reaction was monitored by glc,[16] an early buildup of I followed by its subsequent diminution in favor of XV was noted. Thus after 5 min, the relative percentages of XVI:I:XV are 71:29:<1. There is no evidence for a direct (bridged mode) pathway from XVIa → XVa. Rather, we formulate the transformation of XVIa to XVa in terms of the equilibrium of XVIa with Ia and fused mode reaction of Ia → XVa.

While a variety of reactions are known in which cyclobutane rings are cleaved under less severe conditions than those required for fragmentation of other carbon–carbon single bonds,[17] nucleophilic displacement of the type implicit in the reversion of XVIa to I is, to our knowledge, without precedent.

For the case of Ia, both the spiro and fused mode reactions are competitive. The kinetically complicating reversibility of the former mode is advantageous from a synthetic standpoint since it allows for construction of the 1,3-difunctionalized cyclopentane, XV, in one step from I in reasonable yield.

A full kinetic analysis of this interesting series of ring transpositions will be the subject of a future disclosure. The essential data, summarized below, reveal a preference for the spiro mode[18] of attack ($k_2/k_3 \cong 2.5$) even though it involves formation of a cyclobutane rather than a cyclopentane by apparent nucleophilic displacement at a secondary rather than primary carbon. A similar trend has been noted in opening of epoxynitriles.[5b] The preference may lie in a greater facility for backside[19] attack *via* the spiro mode. It is also possible the increased substitution may be advantageous in promoting polarization of the cyclopropane bond in the direction required for reaction.[20]

(12) R. L. Kroenthal and E. I. Becker, *J. Amer. Chem. Soc.*, **74**, 1056 (1952).

(13) (a) M. Smith in "Rodds Chemistry of Carbon Compounds," Vol. IIA, American Elsevier, New York, N. Y., 1967, Chapter 1; (b) A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc. B*, 67 (1968).

(14) The partial stability of XVII even to the severe reaction conditions stands in contrast with the nondetection of similar proposed intermediates conjugate base of XVIII due to the constraints of the bridged system.

(15) W. R. Vaughn, R. Caple, J. Caspella, and P. Scheiner, *J. Amer. Chem. Soc.*, **87**, 2024 (1965).

(16) The analytical glc separation was conducted on a 10 ft × 1/8 in. 3% OV 225 column at helium pressure = 25 ml/min. The mixture is injected at 70° at an oven program of 1°/min to a ceiling of 190°. The retention times (sec) are XVI = 7350, XV = 7940, and I = 8030. Preparative glc was only possible for the separation of XVI from XV + I. This was achieved on a 20 ft × 3/8 in. SE-30 column isothermally at 150° for 10 min and programmed for 10°/min until a ceiling of 200°. The retention time of XVI is 26 min. The mixture of XV + I has a retention time of 30 min under these conditions.

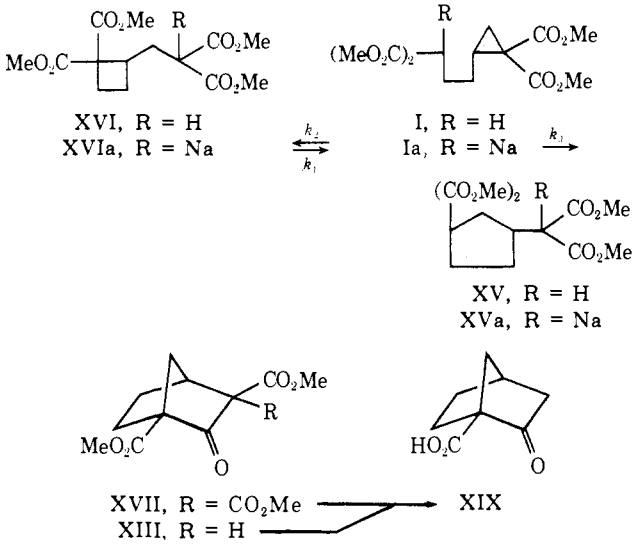
(17) (a) Cleavage of α,α′-dibromo ketones, B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 2038 (1973); (b) hydrogenolysis, J. Newham, *Chem. Rev.*, **63**, 123 (1963); (c) retro-Aldol reaction, P. deMayo, *Accounts Chem. Res.*, **4**, 41 (1971); (d) retro-Dieckmann reaction, G. A. Swan, *J. Chem. Soc.*, 1039 (1955); (e) retro-Michael reaction, E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **83**, 4867 (1961); (f) retro-Prins reactions, J. Hurst and G. Whittam, *J. Chem. Soc.*, 2864 (1960).

(18) For exclusive fused mode attack at room temperature in the case of the corresponding epoxide, see P. A. Cruickshank and M. Fishman, *J. Org. Chem.*, **34**, 4060 (1969).

(19) L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chem. Acta*, **53**, 2050 (1970).

(20) (a) E. W. Yankee, F. D. Badea, N. E. Howe, and D. J. Cram, *J. Amer. Chem. Soc.*, **95**, 4210 (1973); (b) E. W. Yankee, B. Spencer, N. E. Howe, and D. J. Cram, *ibid.*, **95**, 4220 (1973); (c) N. E. Howe, E. W. Yankee, and D. J. Cram, *ibid.*, **95**, 4230 (1973); (d) A. B. Chmurny and D. J. Cram, *ibid.*, **95**, 4237 (1973); (e) G. Rovnyak, Thesis, University of Pittsburgh, 1970.

Further applications of intramolecular homoconjugate addition are under investigation.



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Incursion of Reversibility in Friedel–Crafts Acylations

Sir:

Friedel–Crafts acylation,[1] in contrast to Friedel–Crafts alkylation, is usually considered an irreversible process,[2] free of rearrangements.[3,4] This difference in behavior was attributed to the resonance stabilization existing between the acyl group and the aromatic nucleus.[2] However, if the acyl group is tilted out of the plane of the aromatic nucleus by ortho substituents, the acylation may become reversible[2,5] (*e.g.*, the Baddeley[6] and the Hayashi[7] rearrangements). Naphthalene systems, by virtue of the dichotomy encountered in their Friedel–Crafts acylations, *i.e.*, α *vs.* β substitution, served as an attractive testing ground for evaluating the mechanisms of these reactions.[8-11] Indeed, *Gore's reversibility concept*,[8,12] which states that the Friedel–Crafts acylation reaction of reactive aromatic hydrocarbons is a reversible process, was expounded with naphthalene used as a typical example.[8] However, experiments designed to detect any rearrangement of α-naphthyl ketones to β-naphthyl ketones under Friedel–Crafts acylation conditions have been mostly unsuccessful.[8,13,14] The recently recorded very few cases of such $\alpha \rightarrow \beta$ rearrangements[15] still fall within the category of ortho substituted acyl derivatives[16] (*vide supra*). Their generality is further diminished by the intramolecular nature of the rearrangements. We report the incursion of reversibility in Friedel–Crafts acylations as revealed most conspicuously in the system of benzoylation of naphthalene in polyphosphoric acid (PPA). We note that intramolecularity and *ortho* substitution[16] are not necessary conditions for violating the "pattern of irreversibility" of Friedel–Crafts acylations in the naphthalene series.

The reaction of naphthalene with benzoic acid in PPA for 8 hr at 70° afforded predominantly 1-benzoylnaphthalene (**1**)[17] with only a small quantity of 2-benzoylnaphthalene (**2**)[17] (**1**:**2** = 15:1).[18] At 120° (10 hr), the ratio of the two isomers was almost equal (**1**:**2** = 54:46). At 140° (8 hr), however, the product distribution was inverted; **2** became the major product (**1**:**2** = 2:3). These results indicate that in this reaction, **1** is the kinetically controlled product while **2** is the thermodynamically controlled product. This conclusion was strikingly verified by treating **1** with PPA at 140° for 10 hr; a significant, overwhelming rearrangement of **1** to **2** was achieved (**1**:**2** = 1:12),[18] together with the formation of appreciable amounts of naphthalene.[19] The reverse isomerization could not be effected over a wide range of temperatures (70–140°), although naphthalene consistently sublimed from the reaction mixtures of **2** and PPA. Thus, the benzoylation of naphthalene both at the α and at the β position is a reversible process. The rationale for the rearrangement of **1** to **2** in PPA is probably associated with the spatial orientation of the carbonyl group *vis-à-vis* the naphthalene nucleus in each of the ketones. In **1**, the *peri*-hydrogen causes a certain amount of tilting of the benzoyl complex out of the plane of the naphthalene nucleus, thus reducing the resonance stabilization in the molecule. Therefore, under thermodynamically controlled conditions (*e.g.*, in PPA at elevated temperatures), the conjugate acid of **1** rearranges to that of **2**. The rearrangement presumably involves a fission of the protonated form of **1** into the intermediate benzoylium ion (or the corresponding mixed anhydride with PPA) and naphthalene, which recombine to provide the protonated form of **2**. It should be noted that the benzoyl-

(1) G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I–IV, Wiley-Interscience, New York and London, 1963–1964.
(2) C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York, N. Y., 1970, p 653.
(3) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965, p 174.
(4) N. L. Allinger, M. P. Cava, D. C. De Jongh, C. R. Johnson, N. A. Lebel, and C. L. Stevens, "Organic Chemistry," Worth, New York, N. Y., 1971, p 358.
(5) D. E. Pearson and C. A. Buehler, *Synthesis*, 455 (1971).
(6) G. Baddeley, *J. Chem. Soc.*, 232 (1944); *Quart. Rev., Chem. Soc.*, **8**, 355 (1954).
(7) M. S. Newman and K. G. Ihman, *J. Amer. Chem. Soc.*, **80**, 3652 (1958).
(8) P. H. Gore in ref 1, Vol. III, p 1.
(9) F. R. Jensen and G. Goldman in ref 1, Vol. III, p 1003.
(10) G. A. Olah in ref 1, Vol. I, p 25.
(11) G. Baddeley, *J. Chem. Soc.*, s99 (1949).
(12) P. H. Gore, *Chem. Rev.*, **55**, 229 (1955).
(13) F. R. Jensen, *J. Amer. Chem. Soc.*, **79**, 1226 (1957).
(14) See, however, R. B. Girdler, P. H. Gore, and J. A. Hoskins, *J. Chem. Soc. C*, 181 (1966), who reported a 3% slow rearrangement of 1-acetyl-2-methoxynaphthalene to 2-acetyl-6-methoxynaphthalene.
(15) I. Agranat and D. Avnir, *J. Chem. Soc., Chem. Commun.*, 362 (1973). (The rearrangement of 7,8-dihydro-13*H*-benzo[5,6]cyclohepta[1,2-*a*]naphthalen-13-one to 12,13-dihydro-5*H*-benzo[4,5]cyclohepta[1,2-*b*]naphthalen-5-one.)
(16) In addition to the "ortho substituent" formally inherent in any α-substituted naphthalene.
(17) H. A. Hammond, J. C. Doty, T. M. Laakso, and J. L. R. Williams, *Macromolecules*, 3, 711 (1970).
(18) The product distribution could be monitored by the following methods: (a) vpc (2 m × 0.25 in. column, 15% SE-30 on 60–80 acid washed Chromosorb W, helium carrier gas, 230°; flow rate 50 ml/sec; retention times 9.5 (1) and 11.2 min (2)); (b) tlc (alumina, petroleum ether (bp 40–60°)–benzene (3:1), R_f(1) 0.35, R_f(2) 0.26); (c) nmr (100 MHz, 8.04 (multiplet, 8-H of 1) and 8.14 ppm (singlet, 1-H of 2) downfield from Me_4Si).
(19) Practically, a disappearance of 1 was realized.