stretch); n.m.r. (deuteriochloroform) aromatic C–H (τ 2.00, 2.12), H–C–O (τ 5.20), aliphatic C–H (τ 7.50–9.10); ratios of band areas, 15:1:10. Volhard analysis for ionic halogen gave an equivalent weight of 472 (calcd. equiv. wt., 454).

Anal. Calcd. for $C_{25}H_{26}BrOP$: C, 66.23; H, 5.78; Br, 17.63. Found: C, 65.78; H, 5.92; Br, 17.52.

Decomposition of 7-Norbornoxytriphenylphosphonium Bromide.—The intermediate (1.0 g., 0.00221 mole) was heated on a vacuum line at 170° for 1 hr. at 0.1 mm. pressure. The distillate had a retention time on vapor phase chromatography which was the same as that of *exo*-norbornyl bromide. Solvolysis of the bromide in a sealed tube at 100° in the presence of aqueous silver nitrate was complete after 48 hr. and the alcohol formed was converted to its *p*-nitrobenzoate, m.p. 110.5–111.5°, which was identical with that of an authentic sample of 7-norbornyl *p*-nitrobenzoate (lit.[38] m.p. 106–107°).

Acknowledgment.—We wish to express our gratitude to the California Resarch Corporation for generous support of our work.

(38) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

Bimolecular Displacement Reactions. II. Reaction of *exo*-Norbornanol with Triphenylphosphine and Bromine

JOHN P. SCHAEFER AND DAVID S. WEINBERG[1,2]

Department of Chemistry, University of Arizona, Tucson, Arizona

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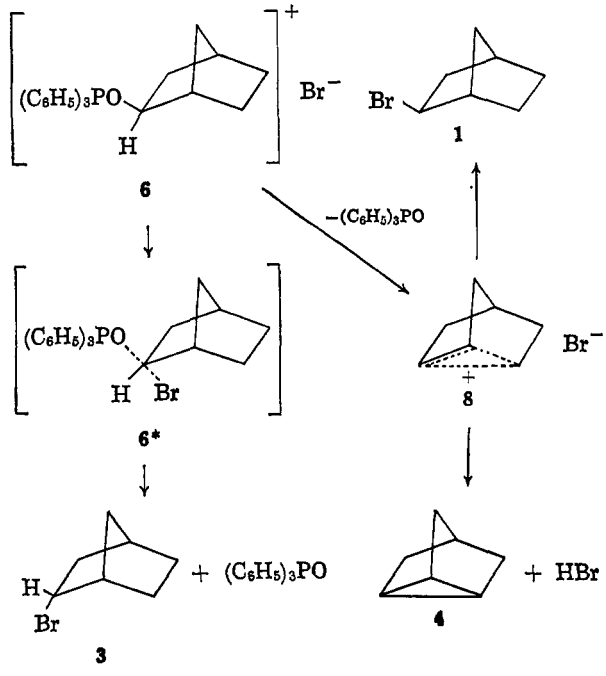
The reaction of optically active *exo*-norbornanol with triphenylphosphine and bromide is solvent dependent and gives 79.1% racemic *exo*-norbornyl bromide, 11.9% of optically active *endo*-norbornyl bromide, and 8.7% of nortricyclene in triglyme; in dimethylformamide these values change to 83.5, 1, and 15.5%, respectively. These data are interpreted in terms of the intervention of the nonclassical norbornyl cation which precipitates a departure in the mechanism of reaction from that which is normally observed.

Displacement of the *endo*-triphenylphosphine oxide moiety by bromide from the norbornyl skeleton provides a practical route to *exo*-norbornyl bromide (**1**) and constitutes one of the few well-documented bimolecular displacement reactions in this system.[3] To determine whether an analogous reaction of *exo*-norbornanol (**2**) with triphenylphosphine and bromine would produce *endo*-norbornyl bromide (**3**), we turned our attention to a further study of this reaction.

When **2** was subjected to experiments parallel to those previously described,[3] the reaction products consisted of 11.9 ± 2% of **3**, 79.1 ± 2% of **1**, and 8.7 ± 0.5% of nortricyclene (**4**) if triglyme was used as the solvent; in N,N-dimethylformamide (DMF) these values changed to 1.0 ± 2, 83.5 ± 2, and 15.5 ± 0.5%, respectively. When optically active alcohol was used, the *exo* halide which was produced was racemic but the *endo* halide was optically active. The marked departure of these results from those observed in the *endo* series requires that a change in mechanism has occurred; since the major products are those reasonably expected from the norbornyl cation,[4] it is evident that a competing path which proceeds through the formation of a carbonium ion has become dominant.

These results, coupled with those obtained with *endo*-norbornanol (**5**), are remarkably similar in many respects to those reported earlier by Winstein and Trifan[5] on the tosylate solvolysis reaction, even though these two reactions would normally be classified at opposite extremes of the spectrum of solvolysis–displacement reactions. Although precise kinetic data have not yet been obtained, the above observations are conveniently accommodated in the mechanistic framework outlined in Scheme I.

SCHEME I
DECOMPOSITION OF
exo-NORBORNOXYTRIPHENYLPHOSPHONIUM BROMIDE



In view of the product structure and the results obtained using optically active **2**, the decomposition of **6** into **3** and triphenylphosphine oxide is obviously the result of a bimolecular displacement process accompanied by a Walden inversion. Alternatively, **1** and **4** must result from a carbonium ion precursor which we have formulated as ion pair **8**. As the dielectric constant of the solvent is increased by changing the reaction medium from triglyme (ϵ ~2) to DMF (ϵ ~37), decomposition of **6** *via* the ion-pair route becomes more favorable as evidenced by the change

(1) Abstracted from the Ph.D. Thesis of D. S. Weinberg, University of Arizona, 1964. Presented at the International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 1964.

(2) National Science Foundation Cooperative Fellow, 1960–1962; Phillips Petroleum Fellow, 1962–1963.

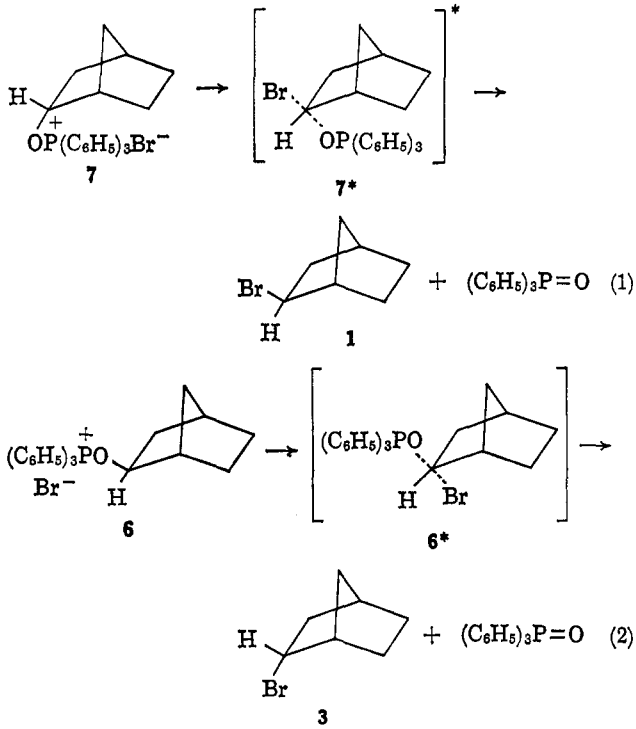
(3) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635 (1965).

(4) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 377 (1965).

(5) S. Winstein and D. S. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

in ratio of products **1** and **4** to **3** from 7:1 to approximately 100:1. These data are noteworthy since even in a solvent such as triglyme, which must be classified as one having a low ionizing power, the majority of **6** decomposes by a process involving a carbonium ion intermediate. Although these data indicate that the triphenylphosphine oxide moiety is an excellent leaving group, an analysis of the bimolecular displacement reaction on the norbornyl skeleton is necessary before the mechanistic change which has occurred can be understood.

The two displacements to be considered are outlined in eq. 1 and 2 and the differences in the free energies of activation for these displacements will be influenced primarily by the relative importance of the interaction of the oxygen moiety with the opposing hydrogens at C-6 and C-7 in the ground states (**6** and **7**) and the transition states (**6*** and **7***) and the similar interactions with bromine in the transition states (**6*** and **7***).



From the limited data in the literature it appears that the free-energy difference between *exo* and *endo* norbornyl derivatives is small but favors the isomer in which the substituent occupies the *exo* position. From a study of the equilibration of the norbornanols[6] using aluminum isopropoxide as the catalyst, K_{equil} was found to be 4.0; for the ethyl norbornane-2-carboxylates the value of K_{equil} is 2.3.[7] Since experience in the cyclohexane ring has shown that in the absence of pronounced branching, it is generally the atom attached to carbon which determines the value of K_{equil}[8] (*vide infra*), it seems safe to conclude that the free-energy difference between **6** and **7** will not differ greatly from that of the norbornanols and will certainly be less than 1 kcal./mole. The primary source of this free-energy difference will be due to the fact that the repulsion between an *exo* substituent and the opposing C-7 hydrogen is less serious than the corresponding repulsion between the *endo* substituent and the appropriate hydrogen and C-6. This factor will enhance the reactivity of **7** relative to **6**.

In the transition states (**6*** and **7***), the geometry of the bridged bicyclic system is such that an increase in the magnitude of these repulsive interactions will occur. A measure of the relative importance of hydrogen–oxygen and hydrogen–bromine 1,3-interactions in molecules is available from the experimental free-energy differences between axial and equatorial substituents determined for cyclohexanes.[8] From a survey of the available data it appears that although these interactions are of the same order of magnitude, the 1,3-interaction between hydrogen and oxygenated groups is generally less favorable than for the similar interaction with bromine. Typical ranges for conformational preferences ($\Delta\Delta F$ values) are Br (0.2–0.7), OH (0.4–0.9), $OCOCH_3$ (0.4–0.7), OCH_3 (0.5–0.7), OC_2H_5 (1.0), p-$OSO_2C_6H_4CH_3$ (0.6, 0.7, 1.7), and p-$OCOC_6H_4NO_2$ (0.9).[8] These data lead to the conclusion that the free energies of **6*** and **7***, and therefore, the free energies of activation for reaction of **6** and **7** by the pathway outlined in eq. 1 and 2, should be of the same order of magnitude. It should be noted that when the nucleophile and *exiphile*[9] are identical, we have a limiting case since both displacements will proceed through the same transition state and the activation energies for displacement of an *exo* or *endo* substituent will differ only by the conformational preference ($\Delta\Delta F$ value) of the group on the norbornyl skeleton.

In view of these conclusions, two interpretations of the decomposition of **6** should be considered. If it is postulated that bimolecular displacement reactions on the norbornyl framework are basically difficult, due to the geometry of the system, and that the shielding influence of the C-6 methylene group is significantly greater than that of the C-7 methylene group, the results can be accommodated into the following scheme. In the case of the *endo* isomer **7** it would follow that departure of the triphenylphosphine oxide moiety would be difficult and would require any assistance available from nucleophilic attack of bromide from the relatively exposed *exo* face of the norbornyl framework. In the *exo* isomer the triphenylphosphine oxide moiety faces no particular barrier to departure, but the C-6 methylene group discourages nucleophilic assistance by bromide so that dissociation to the norbornyl cation occurs. Although this interpretation cannot be excluded rigorously in the absence of kinetic data, we do not believe it is theoretically sound.

After a careful consideration of molecular models and scale drawings[10] it is not apparent to us that the

(6) C. F. Wilcox, M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

(7) A. C. Cope, E. Ciganek, and N. A. LeBel, *J. Am. Chem. Soc.*, **81**, 2799 (1959).

(8) See E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 234, for a comprehensive summary of data.

(9) We propose that the word *exiphile* be used to denote the leaving group. Extensions to *exiphilicity* as a measure of relative leaving ability are obvious and these terms are descriptive and would logically fit in with acceptable chemical nomenclature.

(10) The drawing of the model proposed by Brown and his co-workers[11] is misleading since it is a two-dimensional projection of a three-dimensional molecule and we find that most of the difference in apparent overlap disappears when models of the ion pairs are constructed.

(11) H. C. Brown, F. J. Chloupek, and M. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

shielding capabilities of the C-6 and C-7 methylene groups toward C-2 (and, therefore, their relative influence on reaction rates) are significantly different. Although Corey[12] has summarized the available data on preference for *exo vs. endo* attachment in addition reactions, virtually all of these reactions are complicated by their recognized sensitivity to electronic influences and uncertainties about their transition states such that they cannot realistically be used as a basis for estimating steric effects. Some data which we feel is pertinent is cited below.

In 1937[13] Bode determined the pK_a values of the *exo-* and *endo*-norbornane-2-carboxylic acids. Since ionization constants are very sensitive to the local steric environment of the carboxylate group,[14] owing to inhibition of solvation of the anion, these values provide an estimate of the relative shielding effects of the C-6 and C-7 methylene groups. The pK_a values for the *exo* acid (5.08) and the *endo* acid (5.02) do not differ significantly and suggest that the steric environments of these groups as viewed by solvent do not differ markedly. More significant data are available on the relative rates of saponification of the methyl esters of these acids.[13]

In the transition state for the saponification of an ester, a large increase in the effective volume of the reacting group occurs since the hydroxide ion is adding to the carbonyl group and changing its hybridization from sp^2 to sp^3. In view of the observed ratio of saponification rates (k_{exo}/k_{endo} = 1.7) the differences in the free energies of the activation for the two reactions must be minute.

Further evidence that the C-3 methylene group does not exert an abnormal influence on reactions at C-2 stems from Schleyer's[15] correlation of solvolysis rates which indicates that the solvolysis of *endo*-norbornyl brosylate is normal and is not sterically decelerated. In view of these facts (and those previously cited)[6,7] and the recognized stability of the norbornyl cation,[4,16] we do not believe that an interpretation of our data which relies purely on steric arguments is justifiable or mechanistically sound.

The mechanistic change which occurred during the reaction of **6** is consistent with the availability of an alternative low-energy pathway for reactions of the *exo* intermediate which is not directly accessible to the *endo* isomer and which leads to the direct formation of the nonclassical norbornyl cation (**8**). Formation of **8** is enhanced by the driving force available in the transition state through participation of the C-1–C-6 σ bond[5] in the ionization process. This interpretation suggests that the reactivity of **6** should be greater than that of its *endo* counterpart, **7**; experimental evidence on this point is available from studies on the relative stabilities of the two isomers.

Isolation and purification of **7** gave a white crystalline compound, m.p. 82–83°, which decomposed smoothly at 115° to triphenylphosphine oxide and *exo*-norbornyl bromide.[3] Attempts at comparable studies with the *exo* isomer **6** were less definitive since this intermediate was quite unstable and decomposed rapidly at room temperature. These data, although qualitative, clearly show that **6** is far more reactive than **7**.

A second point of significance is the large percentage of nortricyclene which forms on elimination. Nortricyclene must result from an E1 reaction rather than an E2 process since the percentage of elimination product increases as the dielectric constant of the solvent is increased and, as Kwart[17] has recently shown, norbornene and not nortricyclene is the normal product of the E2 elimination in the norbornyl system. Removal of a proton from a nonclassical intermediate to form norbornene would involve a considerable reorganization of nuclei and electrons to approach a transition state with a favorable stereoelectronic environment for elimination. This reorganization should be relatively expensive in contrast to a transition state in which a simple elimination of a proton from an edge[4] or a face[18] was to occur and, therefore, olefin formation probably cannot compete favorably with cyclopropane formation under the experimental conditions employed.

Experimental[19]

Reaction of *exo*-Norbornanol with Triphenylphosphine and Bromine.—The previously described procedure was followed.[3] Vapor phase chromatographic analyses[20] of the reaction product from *exo*-norbornanol indicated that two components were present. After preparative gas chromatography a waxy solid was isolated whose retention time and infrared spectrum was identical with that of an authentic sample of nortricyclene. Only a trace (*ca.* 1%) of a product having the retention time of norbornene was present and this was subsequently shown to arise from decomposition of a small percentage of the alkyl halide under the conditions of analysis.

TABLE I

ANALYSIS[a] OF PRODUCTS FROM THE REACTION OF ALCOHOLS WITH TRIPHENYLPHOSPHINE AND BROMINE

Source of product	% nortricyclene	% *exo*-norbornyl bromide	% *endo*-norbornyl bromide
exo-Norbornanol (triglyme)	8.7 ± 0.5	79.3 ± 2	12.0 ± 2
endo-Norbornanol (triglyme)[b]	(1.7)	95.7	(2.6)
exo-Norbornanol (DMF)	15.5	83.4	1.1
endo-Norbornanol (DMF)[b]	(1.8)	98.2	(0.0)

[a] The relative amounts of hydrocarbon and alkyl halide were determined by v.p.c. analysis. The relative amounts of the two isomeric alkyl halides were determined by differential kinetic analysis using the Volhard method. [b] The values given are not corrected for the *exo*-norbornanol present as a contaminant. When such a correction is made, each value in parenthesess approaches zero.

(12) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, **84**, 2611(1962).

(13) H. Bode, *Ber.*, **70**, 1167 (1937).

(14) G. S. Hammond and D. H. Hogle, *J. Am. Chem. Soc.*, **77**, 338 (1955).

(15) P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964).

(16) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

(17) H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).

(18) J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76**, 4501 (1954).

(19) Boiling points and melting points (taken in sealed capillary tubes) are uncorrected. Optical rotations were measured with a Rudolph Model 80 high-precision polarimeter. The vapor chromatograms were taken using a 10-ft. 20% Carbowax 20M on firebrick column in a Wilkins Instrument and Research, Inc. Aerograph gas chromatographic instrument or in a similar 5-ft. column in an F and M Scientific Corp. Model 609 flame ionization gas chromatograph. The infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer, the ultraviolet spectra on an Applied Physics Corp. Cary 14 recording spectrophotometer, and the n.m.r. spectra on a Varian A-60 n.m.r. spectrometer.

(20) The chromatographic column employed in this investigation gave the following retention times in a typical analysis at 110°, flow rate 200 cc./min.: technical hexane (second peak impurity), 41.8, 51.2 sec.; norbornene, 93.2 sec.; nortricyclene, 104.5 sec.; *exo*-, and 7-norbornyl bromide, 814 sec.; *exo*- and *endo*-norbornanol, 1345 sec.; and 7-norbornanol, 1490 sec. Various mixtures of the above compounds were completely resolved except for the norbornanols, in which case tailing led to only partial resolution.

TABLE II

POLARIMETRIC ANALYSIS OF REACTION PRODUCTS OF OPTICALLY ACTIVE ALCOHOLS

Source of product	Temp., °C.	Solvent	$[\alpha]^{45}D$, deg.	α (initial)	α (final)[a]	% (+)-*exo*-norbornyl bromide[b]	% (+)-*endo*-norbornyl bromide[b]
exo-Norbornanol (triglyme)	45.0	Aqueous acetic acid–sodium acetate	0.55	0.10 ± 0.02	0.09 ± 0.02	15 ± 20	85 ± 20
endo-Norbornanol (triglyme)	45.0	Aqueous acetic acid–sodium acetate	6.15	0.96 ± 0.02	0.00 ± 0.02	100 ± 2	0 ± 20

[a] The final rotation of the product derived from *exo*-norborneol was measured after two solvolytic half-lives of *exo*-norbornyl bromide. The rotation of the product from *endo*-norborneol was measured after ten half-lives. [b] This crude estimate is based on the assumption that the two isomers have equal maximum rotations and refers to the relative percentages of the two *optically active* isomers present in the reaction mixture.

TABLE III

CONDUCTOMETRIC SOLVOLYSIS OF THE MAJOR PRODUCT OF EACH REACTION[a]

Source of product	10^4k, sec.$^{-1}$
exo-Norbornanol (triglyme)	1.4
endo-Norbornanol (triglyme)	1.4
exo-Norbornanol (DMF)	1.4
endo-Norbornanol (DMF)	1.3
exo-Norbornyl bromide[b]	1.3

[a] Run in 50% aqueous triglyme at 35.1°. [b] This bromide was prepared according to the procedure given by Roberts.[21]

The major component of the reaction mixture was identified as *exo*-norbornyl bromide by a comparison of its retention time, infrared spectrum, and rate of solvolysis with those of an authentic sample. A slower solvolyzing component was also present in the alkyl halide fraction when triglyme was used as the solvent and it was identified as the *endo* isomer since it was optically active when optically active alcohol was used.

The relative amount of *exo*- and *endo*-norbornyl bromides was determined by selective solvolysis in 80% ethanol. It was found that at 90° solvolysis of the *exo* halide was complete in 1 hr. while the *endo* halide required 100 hr. for complete solvolysis and reacted to a negligible degree during the time required to solvolyze the *exo* isomer.[21] The halogen liberated was estimated by the Volhard method.

When reactions were carried out with optically active alcohols, the products were also analyzed by their polarimetric solvolysis rates in aqueous acetic acid containing sodium acetate. All of the results from the above determinations are summarized in Tables I–III.

Attempted Isolation of *exo*-Norbornoxytriphenylphosphonium Bromide.—The identical procedure described for the *endo* isomer was used.[3] Initially the yield of crude product was lower (19 g., 88.5%) and contained much triphenylphosphine oxide in addition to the intermediate. After a 2-hr. evacuation period at 0.5 mm. at room temperature, the residue which remained was primarily triphenylphosphine oxide, m.p. 130–156°, and no longer precipitated from chloroform upon the addition of ether (the intermediate is insoluble in this solvent combination whereas triphenylphosphine oxide is completely soluble); the ultraviolet spectrum was identical with that of triphenylphosphine oxide and markedly different from the *endo* and 7 intermediates. The rapid decomposition of the *exo*-norbornoxytriphenylphosphonium bromide at room temperature indicates that this isomer is much more reactive than the corresponding *endo* derivative.

(21) J. D. Roberts and W. Bennett, *J. Am. Chem. Soc.*, **76**, 4623 (1954)

The Reaction of Ketene with Enamines[1,2]

GLENN A. BERCHTOLD,[3] GEORGE R. HARVEY, AND G. EDWIN WILSON, JR.

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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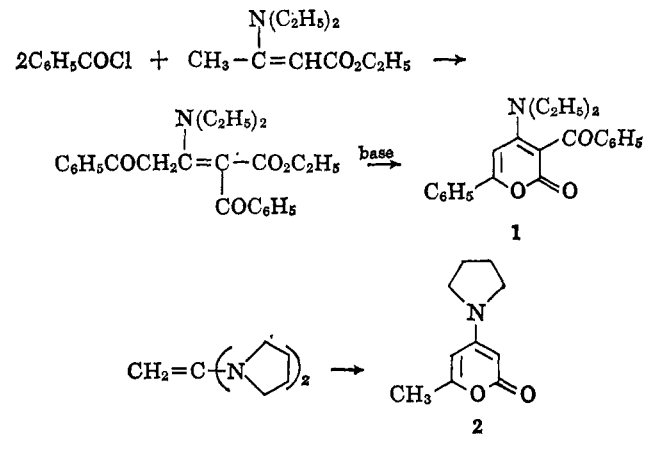
Several enamines derived from ketones have been found to react with excess ketene to yield 2H-pyran-2-ones containing substituents in the 4-, 5-, and 6-positions.

Although the cycloaddition reaction of enamines with 1 equiv. of a ketene or an acid chloride in excess base has received considerable attention as a synthetic route to cyclobutanones,[4,5] little attention has been given to the reaction of enamines with excess ketene to form 2H-pyran-2-ones.[2] Diketene has been observed to react with enamines derived from cyclic ketones to afford 4H-pyran-4-ones.[6,7] The 2H-pyran-2-one **1** has been prepared from ethyl β-diethylaminocrotonate by reaction with 2 equiv. of benzoyl chloride to give ethyl 2,4-dibenzoyl-3-diethylaminocrotonate which cyclized to **1** in base.[8]

This paper is concerned with a one-step preparation of 2H-pyran-2-ones substituted in the 4-, 5-, and 6-positions by reaction of enamines with excess ketene.



(1) This research has been supported by the National Science Foundation, Grant No. G-21443 and GP-1562.

(2) For a preliminary communication on this work, see G. A. Berchtold, G. R. Harvey, and G. E. Wilson, Jr., *J. Org. Chem.*, **26**, 4776 (1961).

(3) Alfred P. Sloan Research Fellow.

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(5) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963); **26**, 4775 (1961).

(6) B. B. Millward, *J. Chem. Soc.*, 26 (1960).

(7) S. Hünig, E. Benzing, and K. Hubner, *Chem. Ber.*, **94**, 486 (1961).

(8) W. M. Lauer and N. H. Cromwell, *J. Am. Chem. Soc.*, **64**, 612 (1942).