Propanol, Dehydro-1,4-dioxane Dimer 19, and the Diesters 17 and 18.—A solution of DMAD (2.0 g, 15.3 mmol) and 1,4-dioxane (10 ml) in acetone (10 ml) was irradiated in a Pyrex tube with a 450-W Hanovia lamp. After 6 hr the photolysis was stopped and the solution was distilled on a steam bath. Glpc analysis of the distillate on both polar and nonpolar columns showed, in addition to acetone and dioxane, the presence of 2-propanol. The residue was chromatographed on a silica column. Earlier eluents with benzene gave white crystals of meso and *dl* forms, mp 155–157° and 131–133°, of dioxane dimer **19**[37] (560 mg) followed by a colorless, fluffy solid, mp 103–110°. The solid could not be crystallized from a host of solvents and is tentatively considered to be a telomer of 1,4-dioxane and DMAD from its spectral data: ir (Nujol) 1725 cm^{-1}; the nmr spectrum in $CDCl_3$ showed a broad singlet at δ 3.7 superimposed on a multiplet at δ 3.6–4.1 and a multiplet at δ 4.6–5.4. Further elution with benzene–ether (4:1) gave a mixture of adducts **17** and **18** as a pale yellow, mobile liquid (550 mg, 18%). The mixture was resolved by preparative glpc.

The major glpc fraction was a colorless liquid and is assigned structure **17**: ir (neat) 1730 (C=O), 1658 (C=C), and 1060 cm^{-1} (ether); nmr (CCl_4, 100 MHz) δ 3.72 and 3.80 (singlets, methyl esters), 3.5–3.9 (m, ring methylenes) (total 12 H), 4.1–4.4 (m, 1 H, ring methine), and 6.20 (s, 1 H, vinylic proton).

Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13; mol wt, 230. Found: C, 52.41, H, 5.97; mol wt, 230 (mass spectrum).

The minor product **18**, which had spectral data similar to those of its isomer **17**, showed in its nmr the vinylic proton as a doublet at δ 6.32 (J = 1.5 Hz). The relative ratio of **17** and **18** in the mixture as determined by areas under its nmr signals at δ 6.2 and 6.32 was 4:1, respectively.

The analytical sample of **18** was obtained by further purification by preparative glpc.

Anal. Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 51.98; H, 6.33.

When DMAD in 1,4-dioxane was irradiated in the absence of acetone for 20 hr only the starting material could be recovered quantitatively.

Photoaddition of DMAD to Tetrahydropyran. Formation of Dimethyl Tetrahydro-2-pyrylfumarate (20) and Dimethyl Tetrahydro-2-pyrylmaleate (21).—A solution of DMAD (2.0 g, 15.3 mmol) and tetrahydropyran (10 ml) in acetone (10 ml) was irradiated with a 450-W Hanovia lamp. Usual work-up after 15 hr gave, in addition to 2-propanol, a mixture of adducts **20** and **21** in a relative ratio of 3.5:1, respectively, as a colorless liquid (1.2 g, 36%). The mixture was separated by preparative glpc.

The major fraction **20** with shorter retention time showed the following spectral data: ir (neat) 1725, 1645, 1070, and 1015 cm^{-1}; nmr ($CDCl_3$) δ 1.3–2.1 (m, 6 H), 3.71 (s), 3.75 (s), and 3.6–4.1 (m) (total 8 H), 5.20 br (t, 1 H, J = 6.0 Hz, C-2 methine proton), and 6.41 br (s, 1 H, vinylic proton).

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 58.11; H, 7.35.

The minor adduct **21** (longer retention time) had the following spectral data: ir (neat) 1730, 1658, 1040, and 1025 cm^{-1}; nmr ($CDCl_3$) δ 1.4–2.1 (m, 6 H), 3.68 (s), 3.72 (s), and 3.5–4.0 (m) (total 8 H), 5.1–5.3 (m, 1 H, C-2 methine proton), and 6.10 (d, 1 H, J = 1.5 Hz, vinyl proton).

Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.69; H, 7.40.

Registry No.—**2**, 762-42-5; **3**, 33536-59-3; **4**, 28864-83-7; **5**, 33536-61-7; **6**, 10486-63-2; **7**, 33522-10-0; **9**, 7370-72-1; **10**, 28864-84-8; **11**, 33522-12-2; **12**, 33536-63-9; **13**, 33536-64-0; **14**, 33522-13-3; **15**, 33536-65-1; **17**, 33536-66-2; **18**, 33536-67-3; *dl*-**19**, 3333-27-5; *meso*-**19**, 3443-36-5; **20**, 33531-70-3; **21**, 33531-71-4.

Acknowledgments.—The author is thankful to Professor Gurbakhsh Singh, Banaras Hindu University, and Professor R. C. Cookson, Southampton University, for providing necessary facilities.

(37) G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963).

The Influence of Structure on the Rate of Thermal Rearrangement of Aryl Propargyl Ethers to the Chromenes. The *gem*-Dimethyl Effect

MORTON HARFENIST* AND EDNA THOM

Burroughs Wellcome Company, Research Triangle Park, North Carolina 27709

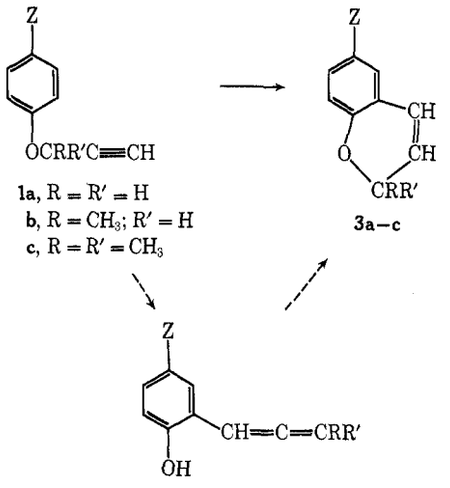
Received July 19, 1971

The rates of first-order thermal cyclizations of a group of para-substituted aryl propargyl ethers *p*-Z-C_6H_4-OCRR'C≡CH with R, R' = H or CH_3 were determined in *o*-dichlorobenzene as a function of Z (OCH_3, NHAc, H, Cl, CN, NO_2) and of the number of CH_3 groups. Where R and R' are both H (*k* values extrapolated to 189.8°) or where R was CH_3 and R' was H (*k* values extrapolated to 161.6°), the points followed an adequate Hammett relationship using σ^+ (ρ = −0.43) although the NO_2 and CN did not give a good fit for R = R' = H, and *p*-Cl was faster than *p*-H for R = H, R' = CH_3. The attempted Hammett plot for the *gem*-dimethyl analogs, R = R' = CH_3, had a paraboloid shape, *e.g.*, X = NHAc and X = NO_2 had about the same rate, with X = H at a minimum (*k* values extrapolated to 161.6°). The $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ followed no obvious order. The results are best explained by assuming that the "*gem*-dimethyl effect" results from an increase in the proportion of the rotamer with the ethnyl group positioned near the benzene ring, *i.e.*, the rotamer best positioned for reaction, when no hydrogen is available to rotate to that position, and that activation of the position meta to the substituent Z, at least by the electron-withdrawing groups, exists. Preparative runs showed that an essentially quantitative yield of 2-methyl- or 2,2-dimethyl-3-chromenes could be obtained in *o*-dichlorobenzene, and this solvent is preferred to *N*,*N*-diethylaniline at least for cyclization of 4-nitrophenyl propargyl ether.

Initial reports[1] of desirable analgetic and related activities of *p*-acetamidophenyl *tert*-butyl ether led us to prepare 3-(4-acetamidophenoxy)-3-methylbutyne [**1c**, Z = $NHC(O)CH_3$]. The method used involved reduction of the corresponding 3-(4-nitrophenoxy) compound **1c**, Z = NO_2, to the amino compound (iron and a trace of acid, with initial purification by steam distillation) and acetylation of that under mild conditions. Although the nitro compound gave the theoretical titer for acetylenic hydrogen, the amino compound produced by this procedure gave a low and variable acetylenic hydrogen titer. Acetylation and purification of the resulting acetylamino compound gave us as a major product in several preparations one or the other of the two isomeric products, one giving the theoretical titer for acetylenic hydrogen, the other giving none. The

(1) See M. Harfenist and E. Thom, *J. Org. Chem.*, **36**, 1171 (1971), for references.

literature available at that time[2] stated that propargyl ethers did not undergo the Claisen rearrangement, but we postulated that a portion of our aminophenyl ether had undergone a Claisen-like cyclization to the chromene **3c**, Z = NH_2, during the steam distillation. The



2

acetamido product was shown to be the chromene, *i.e.*, the result of terminal addition to the ethynyl group, by synthesis by an alternative route of the chroman also made by catalytic reduction and later by nmr. Ionic addition of the nucleophilic benzene ring would have been expected to give the coumaran (five-membered ring) by addition to the internal ethynyl carbon.

After this work had been started, our attention was called to a study of yields in this same reaction.[3] Iwai and Ide concluded from yield data for the pure compound isolated (maximum yield 48% for rearrangement of propargyl ethers) that electron-releasing groups increased the yield, while electron-withdrawing groups gave much lower yields for a relatively constant time. Both statements referred to groups meta to the ethereal linkage, and these authors state that para substituents had no effect on the yield. We studied only para-substituted ethers to avoid any possibility of mixtures of cyclization products. While our studies were under way, other applications of this cyclization were reported.[4]

Our results are based on the rates of loss of acetylenic H. This does not show whether the chromenes **3** are produced directly or the *o*-allenylphenols **2** are produced by a Claisen rearrangement which is rate determining and followed by a rapid ring closure. Gaertner, who first reported[5] the preparation of *o*-allenylphenol **2**, Z = H, found that this compound cyclized readily by a base-catalyzed reaction to give 2-methylbenzofuran when in dilute solution and that it polymerized on attempted isolation. Zsindely and Schmid have shown recently[6] that in the absence of base, *e.g.*, in dilute refluxing benzene solution, *o*-allenylphenol cyclizes rapidly to the chromene. Since our loss of acetylenic hydrogen occurred at a reasonable speed only at temperatures over 100°, this cyclization is several orders of magnitude faster than our measured overall reactions, as would be required for a second step which does not affect the kinetics. Further, thermal rearrangement of di-ortho-substituted phenyl propargyl ethers has given products best formulated as derived from allenic intermediates.

It is stated[7] that the rate of Claisen rearrangements of substituted phenyl allyl ethers follows a Hammett σ^+ relationship. A similar kinetic relationship in our propargyl series would explain the nonrearrangement of the nitro compound during purification by distillation at a distillation temperature comparable to the steam distillation temperature leading to rearrangement of the amino analog. The other factor favoring ready thermal cyclization would be the presence in **1c** of the *gem*-methyl groups.

The existence of a *gem*-dimethyl effect,[8] which increases the rate of cyclization and stabilizes the cyclized products with respect to noncyclic precursors for appropriately-functionalized *gem*-dialkyl compounds as compared with the otherwise identical but unalkylated homologs, is unquestionable. No explanation, however, is universally accepted. Arguments[8b] against one explanation[9] based on bond angle changes seem convincing, at least for *gem*-dimethyl groups. Our own preference is for an explanation based on the relative proportion of rotamers being shifted in favor of rotamers best suited for cyclization, because of the geminal large groups (*vide infra*). However, a third possible explanation is particularly pertinent to our cyclization studies. This[8a,10] postulates that most of the increase of rate due to the *gem*-dimethyl effect is due to an effect on $\Delta F^{\ddagger}$ made up in part of an effect on $\Delta H^{\ddagger}$ due to the increase in gauche interactions on going from the open-chain precursor to the cyclic transition state which more closely resembles product. The increase in $\Delta H^{\ddagger}$ would be less for the *gem*-dimethyl compound which has large ground-state hindrance. In addition, an effect on $\Delta S^{\ddagger}$ is postulated, due to a smaller loss in internal rotations for the *gem*-dimethyl compounds in going to the cyclic form. In the case of our aryl propargyl ethers, the α-methylene group is flanked on one side by an oxygen whose electron pairs are known to offer low nonbonded repulsion[11] and on the other side by the ethynyl group, which at least in the ground state is essentially cylindrical, hence offering a constant, presumably low steric interference to rotation. The influence of the types of nonbonded interactions which Allinger and Zalkow discussed should be minimal in our cyclizations. This should lead to a small if not negligible *gem*-dimethyl effect. Conversely, a *gem*-dimethyl effect caused by increased concentration of the rotamer

(2) D. S. Tarbell, *Org. React.*, **2**, 4 (1944). However, C. D. Hurd and F. L. Cohen, *J. Amer. Chem. Soc.*, **53**, 1068 (1931), indicated that cyclic products formed, among others, on attempted Claisen rearrangement of phenyl propargyl ethers.

(3) I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **11**, 1042 (1963).

(4) (a) B. S. Thyagarajan, K. K. Balasubramanian, and R. B. Rao, *Tetrahedron Lett.*, **21**, 1393 (1963); *Tetrahedron*, **23**, 1893 (1967); (b) J. Hlubucek, E. Ritchie, and W. C. Taylor, *Tetrahedron Lett.*, **17**, 1369, (1969), report excellent yields of *gem*-dimethyl chromenes; (c) Y. Basace and I. Marszak, *Bull. Soc. Chim. Fr.*, 2275 (1971).

(5) R. Gaertner, *J. Amer. Chem. Soc.*, **73**, 4400 (1951).

(6) J. Zsindely and H. Schmid, *Helv. Chim. Acta*, **51**, 1510 (1968).

(7) (a) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Amer. Chem. Soc.*, **80**, 3271 (1958); (b) H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958).

(8) For leading references, see (a) N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, 701 (1960); (b) F. G. Bordwell, C. E. Osborne, and R. D. Chapman, *J. Amer. Chem. Soc.*, **81**, 2698 (1959).

(9) Summarized by G. S. Hammond, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 425, *et seq.*

(10) This summarizes only that part of ref 8a of direct concern here.

(11) See E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970), in which the axial electron pair on oxygen shows a smaller nonbonded repulsion than does axial hydrogen on carbon.

favoring cyclization when the methyl groups are present, would still be important for our propargyl ether cyclizations.

We therefore studied the rates of thermal cyclization of a variety of para-substituted phenyl propargyl ethers in *o*-dichlorobenzene to determine first whether the effect of substituent on rate followed a Hammett relationship and second whether any connection could be found between rates, the number of methyl groups on the saturated carbon of the propargyl group, and the values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$.

The propargyl ethers required were made by the procedures listed in Table III, which also lists properties of the new ethers. All were purified by base extraction to remove any phenols, followed by distillation or recrystallization, and then gave correct elemental analyses. Those which still had less than 95% of theoretical titer for acetylenic hydrogen, as well as all of the dimethyl propargyl ethers made from the phenol salts and 3-methyl-3-chlorobutyne, were purified by way of the silver salt. This was done lest allenic impurities rearrange to acetylenes during the kinetic runs; although normally the kinetic form of a first-order reaction would not be affected by impurities, formation of acetylenes from any allenes present during kinetic runs would have distorted our kinetics. All compounds gave clean first-order kinetics.

Results of Preparative Significance.—Because yields below those required for meaningful kinetics have been reported[3,4] for related reactions recently, it is important that our kinetic data is validated by yields obtained by preparative runs essentially under the conditions of the kinetic runs. Table I shows yields determined by glpc,

TABLE I
YIELDS OF CYCLIZED CHROMENE BY GLPC AND ISOLATED YIELDS[a]

Substituent			Per cent of theoretical by glpc[a]			
Para	R	R′	Product	Starting material	Glpc corrected yield, %	Isolated[a] yield, %
H	H	H	45.5	20.5	66	66
CN	H	H	75	27	102	
Cl	H	H	78	21.4	99.4	36[b]
OCH_3	H	H	71.3			76[b]
NO_2	H	H				46[c]
H	H	CH_3	91	9.0	99	53.5
Cl	H	CH_3	100		100	
OCH_3	H	CH_3	100		100	56[b]
CN	H	CH_3				99[d]
NHAc	H	CH_3				70
NO_2	H	CH_3				84
H	CH_3	CH_3	90		90	
OCH_3	CH_3	CH_3	100		100	83
NO_2	CH_3	CH_3	90		90	75
NHAc	CH_3	CH_3				96
CN	CH_3	CH_3				100[b]

[a] Blanks represent data not determined. [b] Isolated yield by distillation from *o*-dichlorobenzene. [c] Reference 3 reported that none of the chromene resulted from attempted cyclization in diethylaniline under reflux. [d] Sublimed.

and yields of chromene isolated analytically pure, from the cyclization of representative aryl propargyl ethers. While the yields of isolated pure chromene vary with the ease of separation from *o*-dichlorobenzene of the different chromenes, all yields of chromenes determined by glpc were over 90% both for cyclization of the monomethylpropargyl ethers **1b** and for the cyclization of the dimethylpropargyl ethers **1c**. The nonmethylated propargyl ethers **1a** gave lower yields of chromene in two of the four cases studied, together with much resinous material. However, reheating the isolated chromenes for further periods gave tar formation at a sufficiently fast rate to account for the deviation from near-quantitative yield in the cases studied, indicating that the rate of loss of acetylenic hydrogen which was measured in the kinetic runs corresponded in all probability to formation of the chromene and that tar formation was a subsequent reaction of the chromene.[12] Representative chromenes appeared as pure single substances to glpc and tlc and gave the expected pmr after the thermal cyclizations.

An interesting result, which might be of preparative significance but which we did not investigate further, is that we isolated a 46% yield of pure 6-nitrochromene from cyclization of its acetylenic precursor in *o*-dichlorobenzene, whereas Iwai and Ide[3] report only decomposition on attempted cyclization of 3-(4-nitrophenoxy)propyne in refluxing *N*,*N*-diethylaniline. Since *N*,*N*-dialkylanilines are preferred solvents in the true Claisen rearrangement because they diminish the amount of resinification, this result, if it can be confirmed and generalized, would represent a preparatively important difference between the propargyllic ether rearrangement and the true Claisen rearrangement.

Cyclization Rates and Derived Data.—The rates of cyclizations were determined in *o*-dichlorobenzene by titimetric loss of acetylenic hydrogen. This was followed in all cases (except the two indicated) through at least six and generally eight half-lives. In a few cases, the less precise nmr rates were used to check particular points, by determining the ratio at timed intervals of the pmr integral for the *C*-methyl hydrogens of the propargyl ethers (downfield) to the sum of that plus the integral of the *C*-methyl hydrogens of the chromenes produced. Excellent first-order kinetics was found in all cases.

Although it seemed unlikely that first-order kinetics was found fortuitously, this was checked. One cyclization, that of 3-(4-acetamidophenoxy)propyne, was run at three dilutions differing by a factor of 5. All of these gave k values within 2% of the mean. Two runs of the corresponding 4-nitrophenoxy compound differing in concentration by a factor of 2.5 also agreed in k to ±1%. Three runs each with 3-(4-acetamidophenoxy)-3-methylbutyne and the corresponding nitro compound with concentrations differing fivefold had k values differing by 3.8 and 2.6%, respectively, from the mean.

The titimetric rate constants are tabulated in the Experimental Section for the temperatures used, which were three or more temperatures over a range of 30° or more. For rate intercomparisons, it was desirable to compare rates under identical conditions. Therefore, the rate constants found for the cyclization of the nonmethylated ethers **1a** in Table II were extrapolated to 161.6° by the usual linear plot of log k *vs.* $1/T_{abs}$ to facilitate the comparison with the rates of cyclization of the methylated homologs given later. A Hammett plot for the rates of these same cyclizations is shown in

(12) R. Hug, G. Frater, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **54**, 306 (1971).

TABLE II

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THERMAL CYCLIZATION OF COMPOUNDS 1, EXTRAPOLATED TO STANDARD TEMPERATURES

R	R′	Z	$k \times 10^6$, sec^{-1} at 161.6°	Relative rate	$k \times 10^6$, sec^{-1}, at 189.8°	$\Delta H^{\ddagger}$, cal/mol	$\Delta S^{\ddagger}$, eu/mol
H	H	OCH_3	1.15	4.6	18.7	38,700	2.6
H	H	$CH_3C(O)NH$	1.14	4.5	13.4	34,100	−8.0
H	H	H	0.962	3.8	8.71	30,400	−17
H	H	Cl	0.722	2.9	6.74	30,800	−17
H	H	NO_2	0.252	1	5.38	42,600	8.4
H	H	CN	0.245	1	3.25	35,800	−7.2
CH_3	H	OCH_3	9.98	40		33,600	−5.0
CH_3	H	$CH_3C(O)NH$	7.57	30		32,100	−9.0
CH_3	H	H	3.49	14		35,900	−1.7
CH_3	H	Cl	3.79	18		36,100	−1.0
CH_3	H	NO_2	2.27	9.1		38,300	3.1
CH_3	H	CN	2.59	10		33,100	−8.7
CH_3	H	NH_2	50[a]	200[a]			
CH_3	CH_3	OCH_3	628	2500		34,700	5.8
CH_3	CH_3	$NHC(O)CH_3$	402	1600		25,700	−16
CH_3	CH_3	H	203	810		30,000	−7.2
CH_3	CH_3	NO_2	350	1400		34,000	3.1
CH_3	CH_3	CN	250	1000		34,000	2.5
CH_3	CH_3	NH_2[b]					

[a] Crude nmr rate in dimethylaniline. [b] Crude nmr rate in dimethylaniline at 130° was 80×10^{-6}; in trimethylene glycol at 130°, a crude rate determination by nmr gave $k = 250 \times 10^{-6}$.

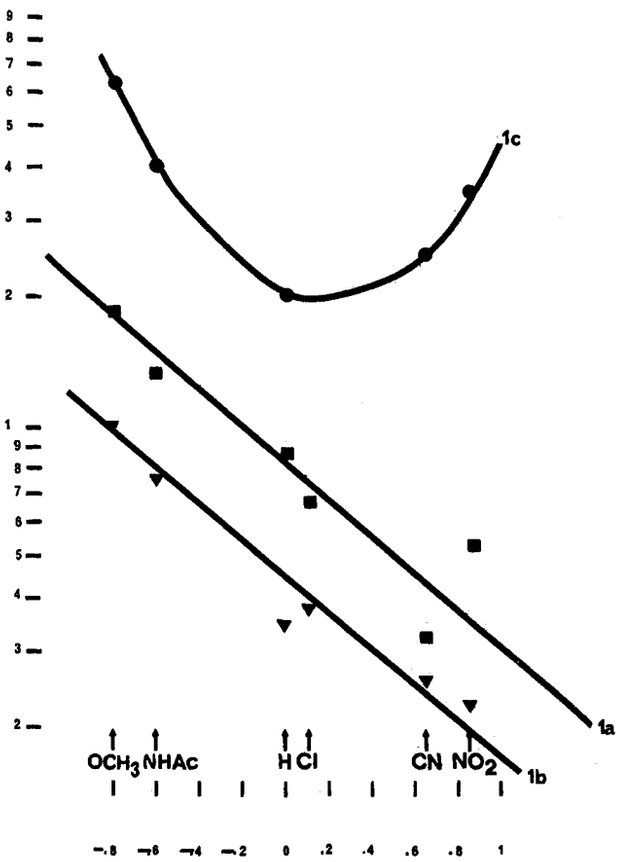


Figure 1.

Figure 1, using k values extrapolated to 189.8°, which is within the range of temperatures actually used for these cyclizations, to preclude significant distortions due to extrapolation. It is evident that σ^+ values[13] give an excellent fit for the electropositive methoxy and acetamido functions, for para hydrogen and for the weakly electron-attracting *p*-chloro substituents, and a poor but perhaps adequate fit for the strongly electronegative *p*-cyano and *p*-nitro groups. Neither the σ_m nor the σ_p values give an adequate fit for these values. This corresponds to the results reported for the Claisen rearrangement[7] both with respect to the magnitude of ρ (−0.43 here *vs.* −0.61 or −0.51) and in the better fit of the Hammett σ^+ relationship shown for electron-releasing substituents than for electronegative substituents here and in the Claisen case.

This Hammett relationship is also satisfactory when the rates of thermal cyclization of the monomethylpropargyl ethers **1b** are examined. Table II shows these rates extrapolated to 161.6°, which for these compounds is within the actual temperature range used for their cyclization. It is apparent, however, that, while the electropositive *p*-methoxy substituent again confers the highest rate of cyclization in this group, the rate of cyclization of the monomethylpropargyl ether with the electron-withdrawing *p*-chloro function is now slightly *faster* than that of the para-unsubstituted analog. A Hammett plot (Figure 1, curve **1b**) can still be drawn to give an excellent straight line, but a line holding all of the other data nicely has the *p*-H and *p*-Cl substituted points below it. This effect is even more marked for the *gem*-dimethylpropargyl ethers **1c**, where the *p*-methoxy leads to the highest rate, but the rates of the *p*-nitro and the *p*-acetamido ethers are nearly the same, both nearly twice as fast as the rate of cyclization of the unsubstituted **1c**, and even the *p*-cyano ether cyclizes faster than the unsubstituted analog, all again extrapolated to 161.6°.

Table II also gives the values found for the energies and entropies of activation.[14] No correlation of either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ values with the degree of methylation at the propargyllic carbon is evident.

Discussion of Rate Results.—The relative rate in-

(13) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958); **80**, 1913 (1958); Y. Okamoto, T. Inukai, and H. C. Brown, *ibid.*, **80**, 4969 (1958); G. Illuminati, *ibid.*, **80**, 4941 (1958).

(14) Values of constants, etc., from J. F. Bunnett, *Tech. Org. Chem.*, **8**, 200 (1961). Note that eq 6 is subject to misinterpretation as type set.

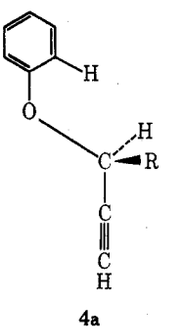
crease going from a given para-substituted monomethylpropargyl ether **1b** to the corresponding *gem*-dimethyl homolog **1c** is greater in all cases than the increase going from any unmethylated ether **1a** to the corresponding **1b**. Further, the increase in rate due to methyl substitution at the propargyl carbon outweighs that of profound change in the "electronic" character of the para substituent. These data are taken to show that this effect of methyl groups is steric, rather than being to any appreciable extent due to stabilization of positive charge on the ethereal oxygen. The low Hammett ρ value found for the undistorted (see below) cyclization of the unmethylated propargyl ethers also shows the small effect of electronic factors.

The obedience to a Hammett relationship and the similarity to the Claisen rearrangement make it likely that the cyclizations of the unmethylated propargyl ethers **1a** represent a valid model of the unperturbed reaction. It then is necessary to explain the deviations from this behavior in the methylated cases. Examination of space-filling models shows appreciable interference between the propargyllic methyl groups and the ortho hydrogen of the benzene ring, although the models can be rotated, more easily for the monomethyl compound models, to positions where the interference appears negligible. The obvious explanation of the relative increase in rate found for the dimethylated ethers **1c**, when Z is electron withdrawing, involves steric hindrance to the coplanarity required at the oxygen for electron withdrawal. The data do not allow a choice between interference with coplanarity due to twisting about the bonds to oxygen and that due to bending of these bonds. The para electron-withdrawing groups should shorten the aryl-to-oxygen bond,[15] but it is uncertain whether this would occur to an extent sufficient to significantly increase the *C*-methyl hindrance. If this steric interference were the only factor, the rates of cyclizations for **1c** when Z is electron withdrawing would approach rather than exceed the rate of the para-unsubstituted analog with the same number of methyls. The fact that the rates of these reactions are *faster* than the Z = H reactions requires that activation of the aryl position ortho to oxygen, which is meta to the electron-withdrawing groups, is also present. This could be electrostatic[16a] in origin and so not subject to steric hindrance effects para to the Z groups. Being an inherently small effect, this meta activation would not be noticeable, except in those cases where the para electromeric effect was minimized, *i.e.*, especially for the *gem*-dimethyl ethers **1c**. It is obvious that the formation of positive charge at the ethereal aryl carbon in the transition state (as shown by the obedience of cyclization rates to a σ^+ relationship) requires development of corresponding negative charge elsewhere in the molecule, for a unimolecular reaction. The electrostatic activation of the carbon meta to the substituent would then suggest that much of this negative charge is present at that carbon in the transition state. Alternatively, this meta activation effect could be present with all of the substituents, but only noticeable for the electron-withdrawing ones. This would be the case if it were due to stabilization of a "free-radical-like" transition state.[17] It is well known[16b] that free-radical-type reagents preferentially substitute in the ortho and para positions to the existing substituent in monosubstituted benzenes. This is attributed to the stabilization of the odd electron in the meta position by delocalization into the substituent. Application of this reasoning to the Claisen rearrangement has been presented.[17] A third alternative, that the electron-withdrawing substituents cause a change in mechanism in the dimethyl cases only, is considered less likely.

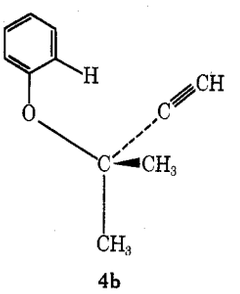
No definite reason is offered as to why our activation parameters, in particular the $\Delta S^{\ddagger}$ values, vary over such a wide range. Variation of ± 4–6 cal/mol would be expected, due to experimental error. It is likely that these reactions are not wholly "adiabatic,"[18] *i.e.*, that more than a single potential energy surface is involved in progress along the reaction coordinate.[19] It is conceivable that the structural differences would affect the crossing over, or lead to a different proportion of "free-radical" character in the transition state. Either of these might lead to a different factoring of $\Delta G^{\ddagger}$ into $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ terms even for compounds with similar rates.

gem-**Dimethyl Effect.**—Our data show a large increase in the rate of cyclization caused by replacement of the geminal hydrogens by methyl groups. This of course is contrary to predictions based on the model for the *gem*-dimethyl effect in ref 8a, provided the flanking oxygen and ethynyl groups show the anticipated low steric interference.

Our suggestion as to the origin of the *gem*-dimethyl effect is that it is largely conformational. Thus **1a–c** would exist largely as the one of the three possible rotamers (ignoring degeneracy) with the lowest energy. If one (in **1b**) or both (in **1a**) R groups are hydrogen, the rotamer with that H nearer the benzene ring's ortho H (**4a**) would predominate, and the ethynyl group would not be situated in appreciable concentration in a position to react, without overcoming a substantial energy barrier to rotation. However, **1c**, with R = R′ = CH_3, would have the rotamer with the ethynyl group in a better position to react (**4b**), since the methyl groups



4a



4b

(15) V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.*, **63**, 37 (1941); T. F. Lai and R. E. Marsh, *Acta Crystallogr.*, **22**, 885 (1967).

(16) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962: (a) p 92; (b) p 471.

(17) (a) D. K. Black and S. R. Landor, *J. Chem Soc.*, 6784 (1965); (b) R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.*, **87**, 2511 (1965); (c) W. N. White, C. D. Slater, and W. K. Fife, *J. Org. Chem.*, **26**, 627 (1961).

(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 78.

(19) That a low-lying excited state is available which has the transoid acetylenic bond required sterically for a Claisen-like rearrangement was shown by C. K. Ingold and G. W. King, *J. Chem. Soc.*, 2702, 2704, 2708, 2725, 2745 (1953). That the potential energy surface for this state intersects the ground state potential energy surface and that perturbations due to reagent attack can allow radiationless transition between them which otherwise would be quantum mechanically forbidden was shown by calculations of L. Burnelle, *Tetrahedron*, **20**, 2403 (1963).

would be more bulky at least than the ground-state ethynyl group and therefore would be away from the benzene ring. Other factors must be important to individual examples of the *gem*-dimethyl effect, but it seems obvious that this rotational factor is the most important one at least here.

Other Results.—In addition to the rates of cyclization of the *p*-aminophenyl ethers discussed earlier, data obtained by integration of pmr absorptions of the propargyl *C*-methyls as a function of time were used to get other preliminary results. Thus, to investigate the possibility that traces of impurities might disproportionately effect our cyclization rates, the rate of cyclization of **1c**, with Z = NO_2, was checked in dried *N*,*N*-dimethylaniline (DMA) and in DMA saturated with water, in DMA containing 12 or 24% (of the weight of **1c** taken) of α-pyridone or in the stronger base (at least in aqueous solution) *N*,*N*-dimethylbenzylamine. All of these rates were essentially identical. Solvent effects were not studied in any detail, but it was observed that the ratio of rate constants for **1c**, Z = NO_2, at 151° for DMA/*o*-dichlorobenzene (DCB) was 1.2,[20] while that for **1c**, Z = NHAc, was 1.6. The former is probably within the limit of error for the preliminary nmr results, while the latter is not. The ratio of rate constants for **1c**, Z = NH_2, at 130° comparing 1,3-propylene glycol/DCB as solvent was 3. This glycol reacted with the acetamido function and the nitro group at the high temperatures required for cyclization, so no further studies were done with it, but it might be useful in special circumstances.

A single preliminary study of the thermal cyclization of the sulfur analog of **1c**, Z = $NHC(O)CH_3$, gave a compound with no acetylenic hydrogen and the correct elemental analysis, presumably the thiochromene. Since this reaction is being studied by others,[21] we contemplate no further work along these lines.

Having relative data, we looked for evidence of uncyclized phenol in our fastest reactions, those of the amino compounds. We have found that a substance that reduces silver nitrate is present in the partial cyclization products of the 4-aminophenyl ethers. Cyclizations of monomethylpropargyl 4-aminophenyl ether (**1b**), Z = NH_2, followed by uv absorption, showed production and eventual disappearance of a strong absorption band at 335 nm (95% ethanol). We have not succeeded in isolating the intermediate, or an acetylated derivative of it, as yet.[22] Work designed to elucidate the mechanism of these cyclizations is continuing.

Experimental Section

Materials and Preparations.—The *o*-dichlorobenzene used as a solvent was commercial material which was distilled twice, taking a center cut arbitrarily. The propargyl ethers were made by the procedures outlined in Table III. Examples of the preparative methods for these propargyl ethers are given. Table IV gives physical properties of the new chromenes.

Method A. Phenol Potassium Salt plus Propargyl Bromide. 3-(4-Chlorophenoxy)butyne.—A solution of 64.3 g (0.5 mol) of *p*-chlorophenol in 400 ml of dried (CaH_2) *tert*-butyl alcohol was treated under N_2 with 56.5 g (0.505 mol) of potassium *tert*-butoxide and then in two equal portions with external cooling between them, with a total of 70 g (0.59 mol) of propargyl bromide, swirling occasionally. The reaction was allowed to stay for 6 hr and then heated under reflux for 0.5 hr and left overnight. It was then filtered, and the filtrate was distilled down, the residue combined with the ether-insoluble water-insoluble oil from the solids, and the resulting ethereal solution was extracted with 250-ml portions of 1 *N* aqueous NaOH and then with water.

TABLE III

PREPARATION OF PROPARGYL ETHERS AND PROPERTIES OF NOVEL ONES[a]

R	R′	X	Prepn[b]	Mp (*c*) or bp (mm), °C
H	H	OCH_3	A[d]	
H	H	$NHC(O)CH_3$	A, B	117.5–119 (B–H)
H	H	H	A, B[d]	
H	H	Cl	A[d]	
H	H	NO_2	A[d]	
H	H	CN	A	113–114 (A)
H	H	NH_2	E	102–104 (0.2)
CH_3	H	OCH_3	A + C, B + C	45 (1)
CH_3	H	$NHC(O)CH_3$	F	120.5–121.4 (A–W)
CH_3	H	H	B	43 (0.25)
CH_3	H	Cl	A	56–57 (H)
CH_3	H	NO_2	D	96–97 (A–W)
CH_3	H	CN	B	99–100 (A)
CH_3	H	NH_2	E	213.5–214[e] (A–E)
CH_3	CH_3	OCH_3	B + C	58–60 (0.1)
CH_3	CH_3	$NHC(O)CH_3$	F	82–83 (H–E)
CH_3	CH_3	H	B[f]	
CH_3	CH_3	NO_2	D	88–90 (0.05)
CH_3	CH_3	CN	B	29–30.5 (H)
CH_3	CH_3	NH_2	E	78–88[g] (0.06)
				189–190.5[e] (A–E)

[a] Satisfactory analyses (±0.4 for C, H) were reported for all compounds except as footnoted. [b] See text for experimental details and examples. A = the phenol potassium salt plus the propargyl halide; B = the phenol plus the propargyl halide plus potassium carbonate in acetone; C = purification *via* the silver acetylide; D = 4-fluoronitrobenzene plus the potassium salt of the propargyl alcohol; E = reduction of the nitro compound by iron in acidic ethanol; F = acetylation with acetic anhydride in ethanol. [c] Recrystallization solvents: A = ethanol; B = benzene; E = anhydrous ether; H = hexane; W = water. [d] I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **11**, 1042 (1963). [e] Hydrochloride; melting point with visible decomposition. [f] J. Hlubucek, E. Ritchie, and W. C. Taylor, *Tetrahedron Lett.*, **17**, 1369 (1969). [g] Base.

TABLE IV

PROPERTIES OF NEW[a] 3-CHROMENES[b]

R	R′	X	Mp (*c*) or bp (mm), °C
H	H	$NHC(O)CH_3$	63–64 (E–H)
H	H	CN	87–110 (0.1)[d]
H	H	NO_2	74.8–76 (A–W)
CH_3	H	OCH_3	70 (0.075)
CH_3	H	$NHC(O)CH_3$	94.5–96 (A–W)
CH_3	H	Cl	140–141 (26)
CH_3	H	NO_2	66–66.5 (E–H)
CH_3	H	CN	55.5–56 (E–H)
CH_3	CH_3	$NHC(O)CH_3$	126–126.8 (A–W)
CH_3	CH_3	NO_2	71–72 (E–H)
CH_3	CH_3	CN	36–37 (H)

[a] For **3a**, X = OCH_3, Cl, H: see I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **11**, 1042 (1963). For **3b**, X = H: see E. E. Schweizer and R. Schepers, *Tetrahedron Lett.*, **15**, 979 (1963). For **3c**, X = $NHC(O)CH_3$: see British Patent 1,121,307. For **3c**, X = OCH_3: see J. Hlubucek, E. Ritchie, and W. C. Taylor, *Tetrahedron Lett.*, **17**, 1369 (1969). For **3c**, X = H: see *Beilstein*, 4th ed, **17**, 64 (1933). [b] Satisfactory analyses for C, H (±0.4) were reported for all new compounds tabulated. [c] Solvents: A = ethanol; E = anhydrous ether; H = hexane; W = water. [d] Solidified after some time, mp 48–50°. Not recrystallized.

(20) J. F. Kincaid and D. S. Tarbell, *J. Amer. Chem. Soc.*, **61**, 3085, (1939), reported that 10% of DMA had no effect on the rate of Claisen rearrangement in phenyl ether; more polar solvents are stated to increase Claisen rearrangement rates, but rather small solvent effects are the rule.

(21) Professor H. Kwart, private communication.

(22) The uv absorption maxima for what is labeled *o*-allenylphenoxide (anion) were reported in ref 5 to be about 250 and 280 nm, while *p*-aminophenol has uv maxima at about 233 and 300 nm in 95% ethanol.

TABLE V

R	R′	Z	Temp, °C	$k \times 10^6$, sec^{-1}
H	H	OCH_3	190.15	17.2
			190.55	22.3
			201.7	56.7
			210.3	114
H	H	NHAc[a]	170.6	2.46
			190.53	18.1, 16.85, 17.45[b]
			190.45	14.65
			200.9	29.9
H	H	H	180.6	4.49
			190.53	9.35
			200.9	17.6
			201.7	18.9
			210.3	41.1
H	H	Cl	190.15	7.18
			200.55	13.6
			210.3	30.3
H	H	NO_2	180.6	2.00
			190.52	6.17[c]
			200.55	15.2
H	H	CN	180.6	1.47
			190.05	2.94
			200.55	9.01
			200.9	9.22
			210.3	15.7
H	CH_3	OCH_3	150.13	3.36
			151.3	3.91
			160.3	8.40
			169.88	21.5
H	CH_3	NHAc	130.25	0.441
			138.9	0.987
			150.0	2.13
			150.12	2.58
			170.4	15.6
			190.05	86.7
H	CH_3	H	138.9	0.299
			150.13	1.30
			151.13	1.14
			160.6	3.45
			169.87	7.62
			190.05	45.2
H	CH_3	Cl	150.13	1.25
			151.3	1.05
			160.2	3.75
			169.88	10.2
			190.05	46.4
H	CH_3	NO_2[a]	149.95	0.565
			150.3	0.760
			160.1	1.91
			170.17	14.18
H	CH_3	CN	150.3	1.05
			160.6	2.03
			192.3	30.0
			200.3	75.3
CH_3	CH_3	OCH_3	140.65	72.1
			149.87	221
			151.7	256
			160.6	528
			170.55	1440
CH_3	CH_3	NHAc[a]	130.25	36.6
			130.75	41.8
			140.15	74.2[d]
			150.25	167
			160.9	408
CH_3	CH_3	H	140.65	33.6
			141.2	27.2
			149.9	78.7
			151.7	120
			160.9	203
			170.25	344
CH_3	CH_3	NO_2	130.25	15.1
			140.15	45.5[d]
			149.9	105
			160.6	333
			170.5	759
CH_3	CH_3	CN	141.2	34.6
			151.7	95.3
			160.6	231

[a] A very high temperature point omitted. [b] Done at 1:2, 1:5, and 1:10 dilutions, respectively. [c] Dilutions of 1:2 and 1:5 differed by 0.16. [d] Multiple dilutions used. See last paragraph of text.

Drying the ethereal solution ($MgSO_4$) and distillation gave 55 g (66%), bp 67° (0.5 mm) and 49° (0.1 mm). This had 99.8–100.3% of the theoretical titer for C≡CH. It crystallized after some time.

Anal. Calcd for $C_{10}H_9ClO$: C, 66.48; H, 4.94. Found: C, 66.64; H, 5.36.

Method B. Phenol plus the Propargyl Halide and Potassium Carbonate. 3-(4-Methoxyphenoxy)butyne.—A mixture of 45 g (0.36 mol) of *p*-methoxyphenol, 71 g of freshly ignited K_2CO_3, and 500 ml of dried acetone was stirred under N_2 while 40.4 g of 3-bromobutyne was added and under reflux for 20 hr more. It was then filtered and solvent was removed *in vacuo*, taken up in ether, washed with 1 *N* NaOH and then with water, dried ($MgSO_4$), and concentrated *in vacuo*, with bath temperatures in this and the preceding acetone removal not permitted to go over 50°. The residue was 37 g of an oil, with acetylenic H titer under 50%. Since rapid thermal cyclization was anticipated for this compound, it was not distilled at this point but instead purified by silver salt precipitation followed by rapid flash distillation.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.83. Found: C, 75.69; H, 6.95.

Method C. Purification by Silver Salt Precipitation. 3-(4-Methoxyphenoxy)-3-methylbutyne.—A 24-g sample of this ether made by procedure B with 61% of the theoretical acetylenic H titer wss dissolved in 150 ml of 95% ethanol and treated with a saturated aqueous solution of 15 g of silver nitrate. The resulting precipitate[23] was filtered with suction and washed with three small portions of ethanol. It was suspended in 150 ml of water and treated with stirring with 5 ml of HCl and extracted into ether. The ethereal solution was washed with water, dried ($MgSO_4$), and flash distilled *in vacuo* giving 9.5 g with a 97% titer for C≡CH.

Method D. 4-Fluoronitrobenzene plus the Potassium Salt of the Propargyl Alcohol. 3-(4-Nitrophenoxy)-3-methylbutyne.—A 25% suspension of potassium hydride (100 g) in oil was washed with dry toluene, using a fritted glass dip tube and N_2 pressure.

(23) If no precipitate forms, it is necessary to add ammonia to pH 9 (indicator paper).

Then 300 ml of 3-methylbutyn-3-ol was added with vigorous stirring under N_2 during 0.5 hr. The resulting solution was treated with 125 g of *p*-fluoronitrobenzene, added dropwise, and stirred at room temperature until 95% of the base had been consumed (3 days). It was then added to water and extracted with ether. The ethereal extract was washed with 1 *N* aqueous NaOH and then with water and dried ($MgSO_4$). Distillation gave recovered *p*-fluoronitrobenzene, bp 80–92° (10–20 mm), and 37 g of product of bp 80–90° (0.01 mm), a 35% yield.

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.78; H, 4.99.

Method E. Reduction of the Nitrophenyl Ether by Iron in Ethanol. 3-(4-Aminophenoxy)-3-methylbutyne.—The nitrophenoxy compound, 0.1 mol, was dissolved in 120 ml of 95% ethanol containing 4 ml of concentrated HCl, and 50 g (0.86 mol) of electrolytic iron powder was added in portions with stirring, starting immediately to minimize acid-catalyzed destruction of ether. After addition of the iron had been completed (*ca.* 15 min), the mixture was stirred another hour, 4 g of sodium acetate was added, and stirring was continued another hour. The precipitate was removed by filtration with a filtering aid and washed with ethanol. The combined filtrate and washings were concentrated *in vacuo* (aspirator and hot water bath) to ~60-ml volume and partitioned between water (1 l.) and ether (three 200-ml portions), and the ether was rapidly extracted with three 150-ml portions of 1 *N* aqueous HCl. The acidic solutions were basified with NaOH as each portion was separated and then extracted back into ether. The dried ($MgSO_4$) ethereal solutions were stripped of ether using a water bath (never over 80° for the dimethyl propargyl ether) and aspirator.

Typically with these precautions, the 3-(4-aminophenoxy)-3-methylbutyne was produced in 35% of the theoretical yield, with 96% of the theoretical acetylenic H.

Anal. Calcd for $C_{11}H_{13}NO$ (base): C, 75.43; H, 7.43; N, 8.00. Found: C, 75.43; H, 7.60; N, 8.04.

The hydrochloride was prepared in, and recrystallized from, anhydrous ethanol–ether and gave satisfactory elemental analyses.

Anal. Calcd for $C_{11}H_{14}ClNO$: C, 62.41; H, 6.67; N, 6.62. Found: C, 62.00; H, 6.65; N, 6.38.

2,2-Dimethyl-6-acetamidochroman.—Detailed preparations of this both by catalytic reduction of the chromene and by acid-catalyzed cyclization of 2-(3-methyl-2-buten-1-yl)-4-acetamidophenol will be found in British Patent 1,121,307 (1968).

Kinetics.—In general, 2.0-g samples of the ether were dissolved in 10 ml of *o*-dichlorobenzene, and the mixtures were heated when necessary in a steam bath until a homogeneous solution was formed. Then 0.2-ml aliquots were pipetted into ampoules which were flushed with N_2 for several minutes and sealed. Six to eight ampoules were placed in a Haake constant temperature bath, Model FT, containing silicone oil preheated to the selected temperature, and withdrawn singly through 6–8 half-lives, cooled to room temperature, and titrated for acetylenic hydrogen.[24] Total times of at least 4 hr and generally 1–5 days were used to minimize errors in time of cooling. Thermometers graduated to 0.2° (Brooklyn Thermometer Co.) were calibrated with Fisher triple-point standards, assuming the melting point to be identical with the triple point within the accuracy required.

Rate constants were calculated after discarding aberrant points found by manual (semilog paper) plots of log titer *vs.* $1/T_{abs}$ but never more than one point was discarded per run. The k was determined from a least-squares program, LINREG, available from the Program Library, General Electric Computer Time Sharing System, by substituting log titer for Y. All points of ln titer *vs.* time were weighted equally. Correlation coefficients better than 0.95 were regularly obtained.

The rates of thermal cyclization of the compounds 1 to give **3** directly determined are given in Table V, where R, R′, and Z refer to compound 1 structure.

Registry No.—**1a** (X = OCH_3), 17061-86-8; **1a** (X = NHAc), 26557-77-7; **1a** (X = H), 13610-02-1; **1a** (X = Cl), 19130-39-3; **1a** (X = NO_2), 17061-85-7; **1a** (X = CN), 33143-80-5; **1a** (X = NH_2), 26557-78-8; **1b** (X = OCH_3), 33146-82-7; **1b** (X = NHAc), 33143-83-8; **1b** (X = H), 1596-40-3; **1b** (X = Cl), 33143-85-0; **1b** (X = NO_2), 33143-86-1; **1b** (X = CN), 33143-87-2; **1b** (X = NH_2), 33143-88-3; **1c** (X = OCH_3), 33143-89-4; **1c** (X = NHAc), 2109-83-3; **1c** (X = H), 30504-61-1; **1c** (X = NO_2), 2109-84-4; **1c** (X = CN), 33143-92-9; **1c** (X = NH_2), 33143-93-0; **1c** HCl (X = NH_2), 33213-36-4; **3a** (X = NHAc), 33143-94-1; **3a** (X = CN), 33143-95-2; **3a** (X = NO_2), 16336-26-8; **3b** (X = OCH_3), 33143-98-5; **3b** (X = NHAc), 33143-99-6; **3b** (X = Cl), 33143-97-4; **3b** (X = NO_2), 33144-00-2; **3b** (X = CN), 33144-01-3; **3c** (X = NHAc), 19849-34-4; **3c** (X = NO_2), 33143-28-1; **3c** (X = CN), 33143-29-2.

(24) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd ed, Wiley, New York, N. Y., 1963, p 389.

Structure–Basicity Relationships of Sulfonium Ylides

K. W. RATTS

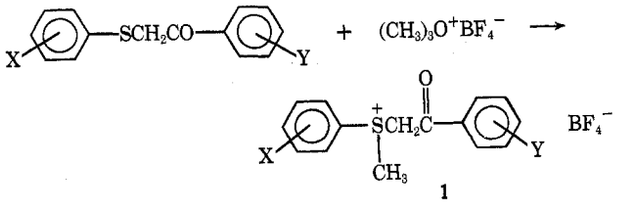
Research Department, Agricultural Division, Monsanto Company, St. Louis, Missouri 63166

Received July 26, 1971

The substituent effect on basicity for a series of arylmethylphenacylsulfonium salts was determined. For the aryl substituents $\rho = +1.13$–1.23 and for the aroyl groups $\rho = +2.63$–2.68. The pK_a values for a series of dialkyl 4-bromophenacylsulfonium salts are directly related to the predicted effect of the S-attached groups on the degree of positive charge on sulfur. The results are interpreted in terms of the effect of various substituents on (1) carbanion delocalization and (2) inductive stabilization *via* the positively charged sulfur group.

The basicity of P ylides is significantly related to their nucleophilicity. A linear correlation between basicity and nucleophilicity has been observed in at least one case.[1] S ylides, however, exhibit no such correlation.[2] To outline fully the factors important to ylide basicity, an understanding of substituent effects is necessary. The purpose of this work is to define the above relationships for S ylides.

A series of methylarylphenacylsulfonium tetrafluoroborates (**1**) was prepared by alkylation of the corresponding sulfides (Table I) with trimethyloxonium tetrafluoroborate.



1

The salts and their pK_a's are listed in Table II. A

(1) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).

(2) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).