dianilide of VI melted at 239–240° (lit.,[4] m.p. 238°).

The cycloaddition of isobutenylamines with other electrophilic olefins, such as acrylonitrile and α,β-unsaturated sulfones and nitro compounds, leads to cyclobutane formation. These reactions, as well as those described above, and some of the transformations of the cyclobutanes will be described in detail at a later date.

We are grateful to Julian H. Chaudet, of these laboratories, for the determination and interpretation of the proton magnetic resonance spectra of compounds II and V. These spectra fully substantiated the assigned structures.

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Gas Chromatographic Separations of Steroids with Polyester Phases

Sir:

The separation of steroids[1] and alkaloids[2] by gas chromatographic techniques has provided a powerful new method for the study of these natural products. The successful use of the method at moderate temperatures (180–220°) depends upon the preparation of a column packing containing a relatively small amount of liquid phase (0.1–3%) coated uniformly on a solid support with an inert surface.[3] Silicone polymer SE-30 was a particularly suitable nonpolar phase.

The value of the method has now been enhanced considerably by the use of polar phases. Preliminary experiments, together with reports[4] of the behavior of thin-film columns used for other purposes, suggested that almost any polar phase could be used in the same fashion as SE-30, provided that the "bleed" rate at 180–220° was low. Five polyesters were selected for study, and columns were prepared in each case with 0.75% phase on Gas-Chrom P.[5] The results are summarized in Table I. The effect of polar phase in each case when compared with SE-30 was an increased relative (to cholestane) retention time for steroids containing polar substituent groups. The magnitude of the effect varied with the structure of the steroid and with the polyester. It is evident that a great deal of choice exists with respect to phases suitable for these separations. The NGS, NGA, and EGIP phases have a high degree of thermal stability, and

TABLE I

Relative Retention Times of 10 Steroids on Columns with Varying Polarity

	Compound	NGA[a]	NGS[b]	EGA[c]	EGS[d]	EGIP[e]
1.	Androstane	0.109	0.112	0.135	0.122	0.175
2.	Androstan-17-one	0.431	0.625	0.765	0.920	0.88
3.	Androstan-3,17-dione	2.48	5.10	7.53	12.5	9.45
4.	Pregnan-3,20-dione	3.30	6.45	9.15	13.7	10.8
5.	Allopregnan-3,20-dione	3.65	7.15	10.1	15.2	12.8
6.	Cholestane	1.00	1.00	1.00	1.00	1.00
7.	Cholestanol-3-methyl ether	2.44	2.74	2.85	2.81	2.77
8.	Cholesterol	5.15	7.30	8.55	8.25	7.20
9.	Cholestan-3-one	5.12	7.05	7.87	7.85	8.38
10.	Stigmasterol	7.30	10.0	12.0	11.4	10.0
	Column size	6′ × 3 mm.	6′ × 3 mm.	6′ × 3 mm.	6′ × 3 mm.	6′ × 3 mm.
	Temp.	210	207	198	200	215
	Inlet pressure, psi.	25	25	25	30	26
	Outlet flow rate, ml./min.	120	120	60	70	65
	Support, mesh	100–140	100–140	140–200	140–200	140–200
	Cholestane time, min.	8.1	4.8	3.5	2.9	3.5

[a] Neopentyl glycol adipate. [b] Neopentyl glycol succinate. We are indebted to Dr. Joseph Corse, Western Regional Research and Utilization Laboratory, Albany, Calif., for a sample of this polyester. [c] Ethylene glycol adipate. [d] Ethylene glycol succinate. [e] Ethylene glycol isophthalate.[1e]

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(1) (a) W. J. A. VandenHeuvel, C. C. Sweeley, and E. C. Horning, *J. Am. Chem. Soc.*, **82**, 3481 (1960) (steroids); (b) W. J. A. VandenHeuvel, C. C. Sweeley, and E. C. Horning, *Biochem. Biophys. Res. Comm.*, **3**, 33 (1960) (sex hormones and bile acids); (c) W. J. A. VandenHeuvel and E. C. Horning, *Biochem. Biophys. Res. Comm.*, **3**, 356 (1960) (adrenal cortical steroid hormones); (d) W. J. A. VandenHeuvel, C. C. Sweeley, and E. C. Horning, *Separation of Steroids by Gas Chromatography*, Symposium on Drugs Affecting Lipid Metabolism, Milan, Italy, June 2–4, 1960 (sterols and sterol esters); (e) C. C. Sweeley and E. C. Horning, *Nature*, **187**, 144 (1960) (steroids); (f) W. J. A. VandenHeuvel, E. C. Horning, Y. Sato, and N. Ikekawa, *J. Org. Chem.*, in press (steroidal amines).

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(3) E. C. Horning, E. A. Moscatelli, and C. C. Sweeley, *Chem. & Ind.* (London), **1959**, 751.

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(5) Applied Science Laboratories, State College, Pa.

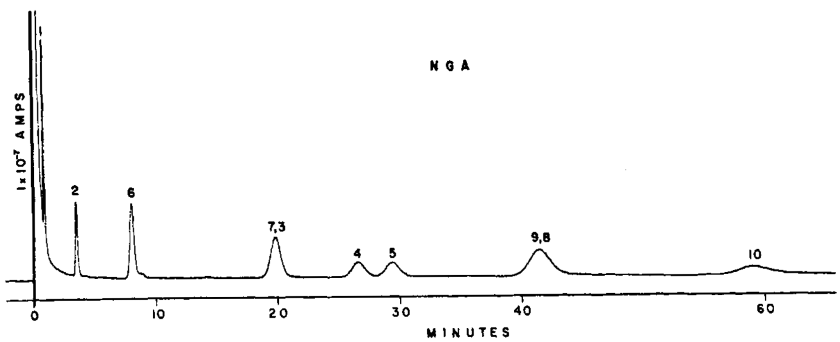

Fig. 1. Separation of steroids with a neopentyl glycol adipate (0.75%) phase on Gas-Chrom P. The conditions and compounds are described in Table I

these may prove to be particularly useful in separation and identification work. Packings with phase concentrations ranging from 0.01 to 10% have been prepared by the filtration technique[3] with these polyesters.

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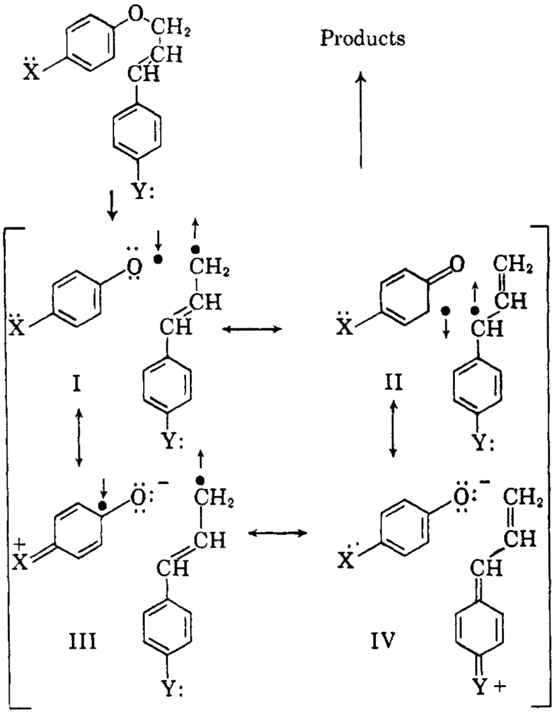
The Electronic Nature of the Transition State of the Claisen Rearrangement

Sir:

Although the Claisen rearrangement has been extensively investigated, the electronic nature of the transition state has not been adequately delineated. For this reason we have made a detailed study of substituent effects on this reaction. The following representation[1,2] is consistent with our experimental findings:



Transition State

It has been shown[3] that the rearrangement rates of allyl *p*-X-phenyl ethers are correlated by Hammett's equation using $\sigma_p{}^+$ constants and a ρ of -0.61 ($r = 0.99$). The isomerization rates of eleven Y-cinnamyl *p*-tolyl ethers were determined spectrophotometrically and are correlated using σ^+ constants and a ρ of -0.40 ($r = 0.99$).

The negative *rhos* indicate that electron depletion occurs in both the cinnamyl chain and the aryloxy portion of the molecule as the reactant changes to transition state. The need for σ^+ constants shows that this electron deficiency interacts directly with the substituent by resonance.

These deductions are accommodated by the proposed transition state. The quasi-radical bond-breaking and bond-forming involves an oxygen atom formally having seven electrons (I). This electron-deficient, electronegative oxygen atom will withdraw electrons from the aryloxy ring (*cf.* III) and the cinnamyl group (*cf.* IV). The electron deficits created in this way would require σ^+ for correlation of substituent effects.[4,5]

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[1] These structures do not imply that actual scission of the molecule into radicals occurs. Structure I is simply the cinnamyl aryl ether with a stretched C—O bond and the γ-carbon in a position to form a long bond to the *ortho* position as indicated in II. Many other contributors of the types shown are possible.

[2] The aryloxy portion of contributing structures I, II, III, and IV are similar to the structures postulated to account for the stability of semiquinones (see G. W. Wheland, *Advanced Organic Chemistry*, 3rd Ed., Wiley, New York, 1960, pp. 802, 803, and 811).

[3] (a) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (3958); (b) H. L. Goering and R. R. Jacobson, *J. Am. Chem. Soc.*, **80**, 3277 (1958).

[4] Similarly thermal cleavage of *t*-butyl X-phenylperacetates (P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 3756 (3960)) required σ^+ constants for correlation probably because of the electronegativity of the oxygen of the *t*-butoxy radical.