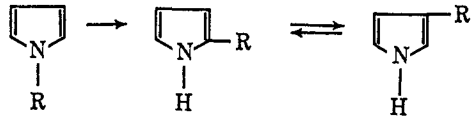
isomer is irreversibly formed from the N isomer while the 3 isomer is reversibly formed from the 2 isomer. Furthermore, the negative entropies of activation calculated from the kinetic data have been interpreted as requiring a cyclic activated complex. Similar results were obtained by Pine[2] in the substituted N-benzylpyrrole series. Since all substituents (F, Cl, CH_3O, CH_3 (*para*)) facilitated isomerization and since activation energies were close to the estimated bond dissociation energies, it was concluded[2] that homolytic dissociation had occurred to the extent of about 90% in the transition state.



We wish to report that the isomerization of N-(*sec*-butyl)pyrrole to the 2 isomer occurred with retention of configuration both above and below the isokinetic temperature of 589°;[3] at 575°, 79% retention; and at 600°, 77% retention. The migration of the phenylethyl group in (+)-N-(1-phenylethyl)pyrrole to the 2 position likewise occurred with 72% retention of configuration at 550°. The 3 isomers, 3-*sec*-butylpyrrole (600° experiment) and 3-(1-phenylethyl)pyrrole, were both formed with an estimated 10% retention of configuration.

N-(*sec*-Butyl)pyrrole,[4] bp 156–156.5°, $n^{25}\text{D}$ 1.4687, $[\alpha]^{25}\text{D}$ +10.2° (neat), synthesized by an adaptation of the method of Elming and Clauson-Kaas[5] from (+)-*sec*-butylamine, $[\alpha]^{25}\text{D}$ +2.5° (neat) (31% optical purity),[6] was pyrolyzed at 575 and 600°. At 575°, 23%[7] of 2-(*sec*-butyl)pyrrole, $n^{25}\text{D}$ 1.4910, $[\alpha]^{25}\text{D}$ +6.38° (neat, 24.4% optical purity) (lit.[8] $n^{25}\text{D}$ 1.4900, $[\alpha]^{25}\text{D}$ +11.24° (43% optical purity)), and 4% of 3 isomer were obtained. At 600°, 31%[7] of 2-(*sec*-butyl)pyrrole, $n^{25}\text{D}$ 1.4910, $[\alpha]^{25}\text{D}$ +6.16° (neat, 23.6% optical purity), and 12%[7] of 3 isomer were obtained. After separation, the 3 isomer was 81% pure, $n^{25}\text{D}$ 1.5010, $\alpha^{24}\text{D}$ +3.92°. Further purification by glpc on an 8 ft × 3/8 in. 30% SE-30 column gave a pure compound, $n^{25}\text{D}$ 1.4870, $[\alpha]^{25}\text{D}$ +8.0° (*c* 2.87, ethanol) (lit.[8] $n^{25}\text{D}$ 1.4878, $[\alpha]^{26}\text{D}$ +11.98° (43% optical purity)). The (+)-*sec*-butylpyrrole has been shown to have the same configuration as (+)-*sec*-butyl bromide[8] and the (+)-*sec*-butyl bromide the same configuration as (+)-*sec*-butylamine.[9]

The pyrolysis of (+)-N-(1-phenylethyl)pyrrole, $n^{25}\text{D}$ 1.5581, $[\alpha]^{25}\text{D}$ +48.15° (neat), synthesized as for the *sec*-butyl compound from (−)-1-phenylethylamine, $n^{25}\text{D}$ 1.5235, $[\alpha]^{25}\text{D}$ −39.7° (neat, 98% optical purity),[10] produced 39.9%[7] of (+)-2-(1-phenylethyl)pyrrole, bp 138–140° (10 mm), $n^{25}\text{D}$ 1.5715, $\alpha^{25}\text{D}$ +62.1°, and 10.9%[7] of (+)-3-(1-phenylethyl)pyrrole, bp 153° (10 mm), $n^{25}\text{D}$ 1.5729, $\alpha^{25}\text{D}$ +9.18°.

The (±)-2- and (±)-3-(1-phenylethyl)pyrroles were synthesized from pyrrylmagnesium bromide and 1-phenylethyl bromide.

The configuration and optical purity of the 2 isomer were established by permanganate oxidation[8] to (+)-hydratropic acid, which in turn was converted into methyl hydratropate and purified by glpc, $n^{25}\text{D}$ 1.4993 (authentic sample, $n^{25}\text{D}$ 1.5000), $[\alpha]^{25}\text{D}$ +79.8° (*c* 4.05, ethanol), 70.5% optical purity. Bonner and Zderic[11] report $[\alpha]^{23}\text{D}$ +108.7° (*c* 5.5, ethanol) for ester prepared from 96% optically pure hydratropic acid. It has been shown by Bernstein and Whitmore[12] that (+)-hydratropic acid and (−)-phenylethylamine have the same configuration.

The configurations of 2-(1-phenylethyl)pyrrole and 3-(1-phenylethyl)pyrrole are probably the same since both isomers give very similar optical rotatory dispersion curves.

It is tentatively concluded that migrations involving considerable free radical character can occur with retention of configuration and that a cyclic transition state is involved in which homolytic bond breaking has progressed to a greater extent than bond formation.

Acknowledgment. The authors thank Dr. E. D. Rees and Mrs. H. Ades for the ORD measurements. The research was supported byt he U. S. Army Research Office, Durham.

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[2] L. A. Pine, *Dissertation Abstr.*, **24**, 522 (1963).

[3] From ref 1. It is assumed that *sec*-butyl group migration follows the same mechanism as do methyl, *n*-butyl, and isopropyl groups.

[4] All new compounds gave satisfactory elemental analyses and all structural assignments were consistent with nmr and infrared spectra.

[5] N. Elming and N. Clauson-Kaas, *Acta Chem. Scand.*, **6**, 867 (1952).

[6] Based on the rotation $[\alpha]^{25}\text{D}$ +8.1° reported by H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964).

[7] Area per cent obtained from glpc analysis on a 6 ft × 1/8 in. 10% SE-30 column. Separations by glpc on an 8 ft × 3/8 in. 30% Carbowax 20M column.

[8] P. S. Skell and G. P. Bean, *J. Am. Chem. Soc.*, **84**, 4660 (1962).

[9] P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold, and P. A. D. S. Rao, *Nature*, **166**, 179 (1950).

[10] Based on the rotation $[\alpha]^{15}\text{D}$ +40.7° reported by W. Leithe, *Monatsh.*, **51**, 381 (1929).

[11] W. A. Bonner and J. A. Zderic, *J. Am. Chem. Soc.*, **78**, 3218 (1956).

[12] H. I. Bernstein and F. C. Whitmore, *ibid.*, **61**, 1324 (1939).

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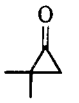
Cyclopropanone[1]

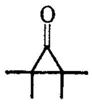
Sir:

The chemistry of small unsaturated molecules of unusual structure is of considerable interest because of both the theoretical predictions concerning the properties of these compounds and their great potential as intermediates in organic syntheses. We report now a relatively simple, high yield synthesis of such a compound, cyclopropanone (**1**). The preparations and reactions of the alkylated cyclopropanones, **2** and **3**, have been reported recently.[1,2]

1



2



3

Addition of a cold (−78°) methylene chloride (10 ml) solution of diazomethane[3a] (10 mmoles) to a methyl-

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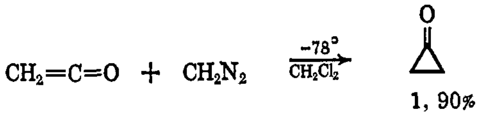
[1] Cyclopropanones. IV. See W. B. Hammond and N. J. Turro, *J. Am. Chem. Soc.*, **88**, 2880 (1966), for paper III is this series.

[2] N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2774 (1965).

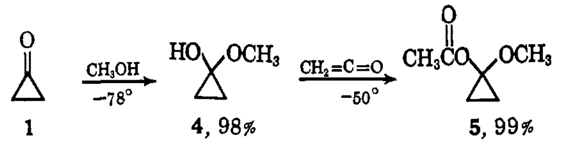
[3] (a) G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965), (b) W. E. Hanford and J. C. Sauer, *Org. Reactions*, **3**, 136 (1946).

ene chloride (5 ml) solution of ketene[3b] (45 mmoles) yields **1** in 90% yield. Removal of the excess ketene by vacuum distillation (−78°) affords pure solutions of **1** (50–60% over-all yields based on diazomethane[4]). Compound **1** shows infrared absorption[5,6] at 3045 (cyclopropane C–H) and 1813 cm^{-1} (strained carbonyl); nmr singlet[7] at τ 8.35; ultraviolet spectrum $\lambda_{\max}^{CH_2Cl_2}$ 3100 ($\epsilon \sim 23$) and 3300 A (infl).



(1)

Addition of CH_3OH to a pure CH_2Cl_2 solution of **1** at −78° affords **4** in 98% yield.[6] If an equivalent amount of CH_3OH is added to **1** *in the presence of a 3–4-fold excess of ketene*, **4** is formed exclusively[8] and

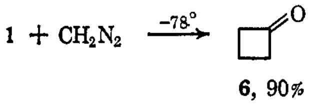


(2)

then is acylated quantitatively by ketene to yield **5**, infrared $\lambda_{\max}^{CCl_4}$ 2832 (OCH_3) and 1745 cm^{-1} (CH_3COO); nmr two sharp singlets at τ 6.44 (three protons) and 7.92 (three protons) and a broadened multiplet centered at τ 9.0 (four protons); mass spectrum *inter alia: m/e* 130 (M^+, very weak), 115 ($M - CH_3$, 3%), 88 ($M - CH_2{=}C{=}O$, 12%), 71 ($M - CH_3COO$, 7%), and 43 (CH_3CO^+, 100%).

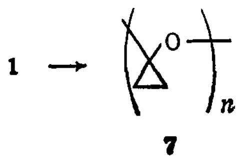
Thus *there is a remarkable difference in reactivity of* **1** *and ketene toward nucleophiles* since **1** is attacked by CH_3OH at least 10–100 times faster than ketene, but ketene is much more reactive toward diazomethane.[9]

Cyclopropanone nonetheless reacts smoothly with diazomethane[6,9] even at −78° to yield cyclobutanone (**6**).



(3)

At room temperature **1** rapidly polymerizes[6] to yield a compound assigned structure **7**: nmr broad singlet at τ 9.1, infrared 1130 cm^{-1} (C–O) and 1050, 980, and 950 cm^{-1} (Δ-C–C stretch).



(4)

This polymerization reaction completes favorably with addition of **3** to dienes such as furan and cyclopentadiene.[10]

Acknowledgment. The authors gratefully acknowledge the generous support of the Air Force Office of Scientific Research (Grant AFOSR-1000-66) and the National Science Foundation (Grant NSF-GP-4280).

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(4) Analysis by nmr of flash distilled solutions of **1**.

(5) A. Kende, Ph.D. Dissertation, Harvard University, Cambridge, Mass., 1957.

(6) P. Lipp and R. Doster, *Ber.*, **64**, 2823 (1931).

(7) Methylene chloride solution, TMS external standard.

(8) No methyl acetate; the product of reaction of ketene and methanol is detectable in the reaction mixture by nmr analysis.

(9) D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, 78, 3221 (1956).

(10) Reaction does occur with more nucleophilic unsaturated compounds such as enamines: W. B. Hammond, unpublished results.

(11) Alfred P. Sloan Fellow.

(12) National Science Foundation Predoctoral Fellow, 1964–present.

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A Generalized Theoretical Basis for the Octant Rule[1]

Sir:

The octant rule for optically active ketones[2] is a generalization giving absolute molecular configuration. The purpose of this note is to report a general theoretical relationship which predicts the correct octant behavior and gives the correct absolute sign of rotatory strength. While this development is part of a larger program for obtaining sector or regional rules for the optical activity of intrinsically inactive chromophores,[3] it seems sufficiently straightforward and important to warrant early notice.

A quantal development for the $^1A_2 \leftarrow {}^1A_1$ (n–π^*) transition rotatory strength of a carbonyl group interacting with a negligibly overlapped nonpolar perturber gives

$$R_{0,n\pi} = +i \sum_{1} 2(E_1^2 - E_{n\pi}^2)^{-1} E_1 (A_{n\pi}B_1|V|A_0B_0)\mu^z_{0,1} m^z_{n\pi,0} \quad (1)$$

Both ground and excited spectroscopic state carbonyl wave functions are perturbed to the first order.

Here $m^z_{n\pi,0}$ is the z component of magnetic dipole transition moment of the isolated carbonyl group, $\mu^z_{0,1}$ is a "borrowed" electric transition dipole moment of the perturber. $(A_{n\pi}B_1|$ represents a product wave function with the carbonyl group A in the upper state of its n–π^* transition and perturber group B in its 1 state. V is the electrostatic potential between the charge distributions of A and B.

Expansion of the perturbation matrix element shows it depends in part on the product of $\theta^{xy}_{0,n\pi}$, the xy component of electric quadrupole transition moment of the isolated carbonyl group, and $\mu^z_{0,1}$. The sum over excited states 1 of the perturber then defines its mean polarizability measured at the n–π^* transition frequency, $\bar{\alpha}(\nu_{n\pi})$, to give[4]

$$R_{0,n\pi} = -15 i \bar{\alpha}(\nu_{n\pi}) R^{-7} XYZ \theta^{xy}_{0,n\pi} m^z_{n\pi,0} \quad (2)$$

R is the distance from carbonyl to perturber centers of gravity; X, Y, and Z are the signed components of that distance on a right-handed coordinate system centered on the carbonyl oriented so that Z is in the C–O direc-

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(1) This work supported in part by Public Health Service Grant GM-11644 and in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

(2) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, 83, 4013 (1961).

(3) O. E. Weigang, Jr., and E. G. Höhn, to be published.

(4) See D. J. Caldwell and G. Eyring, *Rev. Mod. Phys.*, **35**, 577 (1963), where limited sets of one-center hydrogenic wavefunctions describing average electronic properties are used to predict similar behavior.