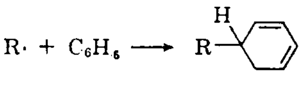
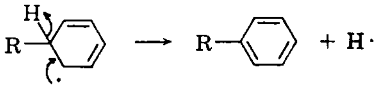
tion can take place with other monomers is still unanswered.

In an attempt to answer this question, we have studied the reactions of what is probably the most reactive polymer radical, the polyethylene growing chain. Ethylene was polymerized to low conversion in a batch reactor at 20,000 psi. and 130° using di-*t*-butyl peroxide initiator. Steady-state polymerization was demonstrated. Vapor chromatography of benzene-C^{14} as obtained diclosed the presence of a number of impurities. The pure benzene-C^{14} used in this study was obtained by trapping the benzene peak. Scintillation counting of the polymer made in the presence of this benzene-C^{14} indicated incorporation of a small but definite quantity of benzene in the polymer. Were this benzene to have been incorporated by chain-transfer with the growing polymer chains, a transfer constant of 9.7×10^{-4} would be calculated. From molecular weight measurements of polyethylenes prepared in the presence of large quantities of unlabeled benzene, a chain-transfer constant of $(9.4 \pm 0.8) \times 10^{-4}$ was obtained. Therefore, chain transfer, not copolymerization, takes place.

In order to give a significant answer to the main question, however, we must know why copolymerization failed in this instance. The reason for failure can be deduced from a knowledge of the mechanism for chain transfer. If transfer occurs *via* direct abstraction of hydrogen (scheme 1) then we can infer that copolymerization fails because the growing polymer chain does not add to benzene. However, if transfer occurs as suggested by Mayo[6] (scheme 2) we would conclude that copolymerization fails after addition of benzene takes place because the intermediate radical loses hydrogen more readily than it adds ethylene. More easily polymerized monomers might then be expected to copolymerize with benzene. Scheme (2) is plausible inasmuch as addition of methyl[7] and trifluoromethyl[8] radicals to benzene has been demonstrated.

$$R\cdot + C_6H_6 \longrightarrow RH + C_6H_5\cdot \qquad (1)$$


(2a)


(2b)

In order to differentiate between the schemes, the chain-transfer constant of deuteriobenzene[9] was determined. The value obtained, $(5.6 \pm 1.1) \times 10^{-4}$, shows a strong isotope effect. If addition to a double bond of benzene (step 2a) were the rate-determining step, only a small isotope effect would be expected. Hence, 2a cannot be the rate determining step. Step 2b should show a large isotope effect. However, for it to be rate-determining, either the polymerization rate would have to be reduced seriously or step 2a would have to be readily reversible. Deuteriobenzene would retard the rate more than benzene. It is our experience that reactions similar to 2a are not reversible. Furthermore, only a slight rate reduction was observed and deuteriobenzene retarded the rate less than benzene. Therefore, scheme 2 cannot be the mechanism of transfer and scheme 1, which fits all the evidence, must be correct. Copolymerization fails because addition to a double bond of benzene does not take place.

In conclusion, we have found that even the highly reactive primary alkyl radical, a growing polyethylene chain, does not add to benzene. When polyethylene chains react with benzene it is by direct abstraction of hydrogen. We therefore believe that free-radical copolymerization of benzene is impossible.

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[6] F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943).

[7] M. Levy, M. Steinberg and M. Szwarc, *ibid.*, **76**, 3439 (1954).

[8] J. L. Holmes and K. O. Kutschke, *Trans. Faraday Soc.*, **58**, 333 (1962).

[9] Supplied through the courtesy of Monsanto Research Corporation which obtained it from Ciba, Switzerland. Mass spectrographic analysis indicated 99.9% C_6D_6.

A NON-CARBENOID RING EXPANSION OF A BENZENOID SYSTEM

Sir:

We wish to report a remarkable one-step ring expansion of a benzenoid system (phenoxide ion) by a species other than a carbenoid entity (chloramine). Although the ambident character of phenoxide ions has been clearly demonstrated in the classical studies of Claisen,[1] Curtin,[2] Kornblum[3] and their associates, attention has been directed only to alkyl, alkenyl and aralkyl halides as alkylating agents.[4] It seemed apparent that the synthetic applicability of this method could be generalized and we were led to investigate the reaction of the sodium salts of 2,6-disubstituted phenols with chloramine. This procedure does not lead to the simple O-arylhydroxylamines,[5] but instead results in the ring enlargement of the phenoxide moiety to give 1,3-dihydro-2H-azepin-2-ones (I) and thus provides a facile synthetic entry into this

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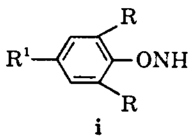
[1] L. Claisen, F. Kremers, F. Roth and E. Tietze, *Ann.*, **442**, 210 (1925); L. Claisen, *Z. angew. Chem.*, **36**, 478 (1923).

[2] D. Y. Curtin and D. H. Dybvig, *J. Am. Chem. Soc.*, **82**, 225 (1962), and leading references contained therein.

[3] N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

[4] A study of the action of sodium 2,6-dimethylphenoxide on perchloryl fluoride has been reported recently; *cf.* A. S. Kende and P. MacGregor, *ibid.*, **83**, 4197 (1961).

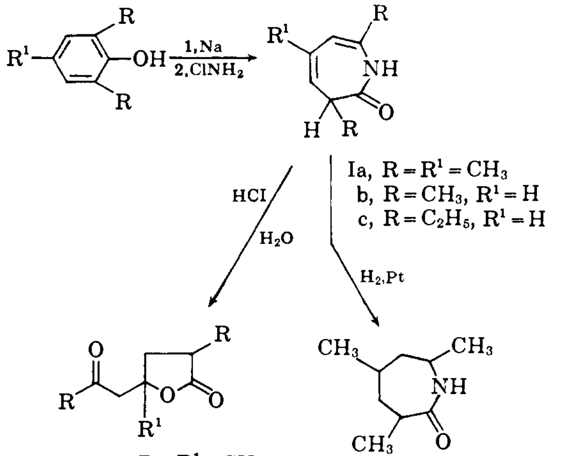
[5] The interaction of phenoxide ions with chloramine has been previously described: (a) W. Theilacker and E. Wegner, *Angew. Chem.*, **72**, 131 (1960); (b) W. Theilacker, *ibid.*, **72**, 498 (1960). Although a direct comparison of samples has not been made, these workers appear to have formulated the reaction products incorrectly as O-arylhydroxylamines (i):


i

little known heterocyclic class[6] (which may be alternatively named dihydroazatropones).

Addition of a cold (−70°) ethereal solution of chloramine[7] in a thin stream to a rapidly stirred solution of sodio 2,4,6-trimethylphenoxide in excess 2,4,6-trimethylphenol at 120–150° affords on appropriate workup[6a] a 50–55% yield of a fluffy white solid [m.p. 132°; *Anal.* Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.68; H, 8.47; N, 9.16; ν_{max}^{Nujol} 3200 (N-H) and 1695 cm.$^{-1}$ (amide carbonyl); λ_{max}^{EtOH} 252 mμ (6,050)]. The n.m.r. spectrum[8] is fully compatible with the 3,5,7-trimethyl-1,3-dihydro-2H-azepin-2-one formulation (Ia); a low field singlet at 334.5 cps. was assigned to the proton at position 6, a doublet centered at 292.5 cps. (J = 5 cps.) to the proton at position 4 and a 5-line pattern centered at 148 cps. (J = 6 cps.) to the ring proton at 3, the pattern suggesting splitting with an adjacent methyl group and ring hydrogen atom. In addition, the absorption peaks of the various methyl groups were located at 120 cps. (singlet, 7-methyl), at 107.5 cps. (triplet, J = 1.5 cps., 5-methyl) and at 80.2 cps. (doublet, J = 6.5 cps., 3-methyl).

Catalytic reduction of Ia with platinum oxide in ethanol proceeded with the uptake of two moles of hydrogen to give 3,5,7-trimethylhexahydroazepin-2-one (II), m.p. 73–75°, in 72% yield. An authentic sample of II was prepared by the Beckmann rearrangement of 2,4,6-trimethylcyclohexanone oxime.[9] Comparison of the spectral and m.p. properties of II with the lower melting isomer[10] from this sequence showed them to be identical.



Ia, $R = R^1 = CH_3$
b, $R = CH_3$, $R^1 = H$
c, $R = C_2H_5$, $R^1 = H$

IIIa, $R = R^1 = CH_3$
b, $R = CH_3$, $R^1 = H$

II

Acid hydrolysis of Ia yielded the keto-lactone IIIa (84%) [b.p. 90° (0.25 mm.) $n^{24.5}D$ 1.4528; *Anal.* Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.32; H, 8.51; ν_{max}^{neat} 1770 (lactone carbonyl) and 1720 cm.$^{-1}$ (ketone carbonyl); λ_{max}^{EtOH} 274 mμ (197)].

In a similar manner, 2,6-dimethylphenol and 2,6-diethylphenol were transformed to Ib and Ic, respectively. IIIb was produced readily when Ib was submitted to acidic hydrolysis.

Further extensions of this novel reaction and the chemical and photochemical transformations of the 1,3-dihydro-2H-azepin-2-ones as well as the mechanism of their formation will be described in forthcoming publications.

Acknowledgment.—The author is indebted to Mr. Douglas B. Hooker for the preparation of the chloramine and to Dr. R. W. Rinehart and staff of the Physical and Analytical Chemistry Department of the Upjohn Company for the microanalytical and spectral determinations.

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[6] E. Vogel and R. Erb, *Angew. Chem.*, **74**, 76 (1962), have described recently a five-step synthesis of this previously unknown ring system.

[7] G. H. Coleman and H. L. Johnson, "Inorganic Syntheses," Vol. I, p. 59.

[8] Spectra were determined by Dr. George Slomp on dilute solutions in deuteriochloroform with a Varian 4300-2 Spectrometer operating at 60 mc. The spectra were calibrated by the audiofrequency sideband technique against internal tetramethylsilane standard (TMS = 0 c.p.s.).

[9] This sequence has been described previously by H. E. Ungnade and A. D. McLaren, *J. Am. Chem. Soc.*, **66**, 118 (1944); *J. Org. Chem.*, **10**, 29 (1945).

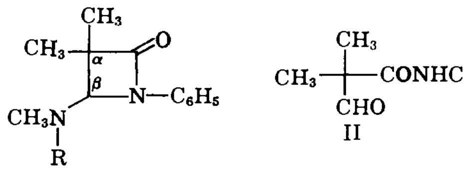
[10] A higher melting isomer, m.p. 95°, also was isolated.

AN ENAMINE SYNTHESIS OF β-AMINO-β-LACTAMS (4-AMINO-2-AZETIDINONES)

Sir:

The cycloaddition of ketenes to Schiff bases was the original preparative method for β-lactams.[1] The present report, concerning the reaction of β,β-disubstituted enamines with aryl isocyanates, constitutes the first β-lactam synthesis in which the carbonyl to C_α and nitrogen to C_β bonds are formed simultaneously.[2] The only other β-lactam synthesis known to the authors which utilizes an isocyanate is the phenyl isocyanate–diazomethane synthesis of Sheehan.[3]

The combination of equimolar quantities of N,N-dimethylisobutenylamine[4] and phenyl isocyanate causes a spontaneous exothermic reaction. The infrared spectrum of the resulting oil shows no absorption at 4.4–4.5 μ, which is characteristic of the isocyanate, but has an intense peak at 5.71 μ. The structure Ia (1-phenyl-3,3-dimethyl-4-dimethylamino-2-azetidinone) which we propose for this reaction product is consistent with the infrared spectrum and further supported by n.m.r. results.



II

Ia, $R = CH_3$
b, $R = C_6H_5$

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[1] Staudinger, "Die Ketene," F. Enke, Stuttgart, 1912.

[2] "The known syntheses of β-lactams that create two bonds all entail simultaneous formation of the same two bonds, *i.e.*, carbonyl to nitrogen and Cα to Cβ": J. C. Sheehan and E. J. Corey, "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 390.

[3] J. C. Sheehan and P. Izzo, *J. A . Chem. Soc.*, **70**, 1985 (1948); **71**, 4059 (1949).

[4] K. C. Brannock, A. Bell, R. D. Burpitt and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961).