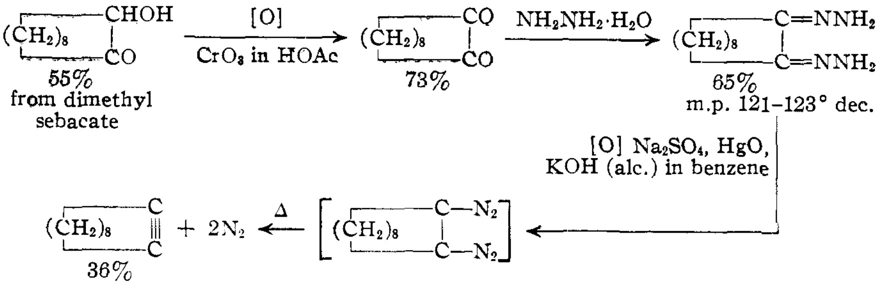
by Domnin[3] in his presumed synthesis of cyclooctyne always seems to have afforded mixtures of cyclic acetylenes and isomeric allenes when applied to the nine- and ten-membered carbon rings. Thus, for example, dehydrohalogenation of 1-chlorocyclononene or dehalogenation of 1-bromo-2-chlorocyclodecene gave a mixture of $C_9H_{14}$ and $C_{10}H_{16}$ hydrocarbons, respectively, which upon ozonolysis yielded a mixture of suberic and azelaic acids or a mixture of azelaic and sebacic acids. Further, the infrared spectrum of the $C_{10}H_{16}$ hydrocarbon mixture showed a very weak absorption at 4.55 μ (C≡C stretching) and a much stronger absorption at 5.16 μ (C=C=C stretching).



However, we have obtained the cyclic $C_9$ and $C_{10}$ acetylenes employing a modification of a method developed by Curtius for synthesizing diaryl acetylenes.[4] The method as applied to the nine- and ten-membered carbocycles is illustrated by the synthesis of cyclodecyne from sebacoin.

The cyclic acetylenes ($C_9$ and $C_{10}$) as first isolated were found to contain small amounts of carbonyl compounds and saturated hydrocarbons but they were not contaminated with allenes or other unsaturated hydrocarbons. Final purification of the two acetylenes was achieved by chromatography through silica gel. Their purification was followed by means of infrared absorption spectra, refractive index measurements, and by quantitative catalytic hydrogenation.

Cyclodecyne was purified by chromatographing through silica gel: b.p. 203–204° (740 mm.), $n^{20}\text{D}$ 1.4903, $d^{20}_4$ 0.8975 (*Anal.* Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.30, 88.06; H, 11.78, 11.98). Quantitative reduction in acetic acid using Adams catalyst required 99–100% of two molar equivalents of hydrogen. Ozonolysis gave only sebacic acid (37%), m.p. 126–129° after recrystallization and the mixed melting point with an authentic specimen of sebacic acid (m.p. 129–131°) was 126–129°. The ozonolysis product was also characterized as sebacic acid by conversion to the bis-*p*-toluidide, m.p. 198–200° (cor.). Hydration of the acetylene with sulfuric acid and mercuric sulfate in acetic acid gave cyclodecanone, isolated as its semicarbazone, m.p. 203.5–205.5° (cor.). A mixed melting point with an authentic specimen showed no depression. The infrared spectrum of the unsaturated hydrocarbon (Fig. 1) showed characteristic absorption for C≡C at 4.53 μ.

Cyclononyne was purified by chromatographing through silica gel: micro b.p. 177–178° (740 mm.), $n^{20}\text{D}$ 1.4891, $d^{20}_4$ 0.8979. (*Anal.* Calcd. for $C_9H_{14}$: C, 88.45; H, 11.55. Found: C, 88.24; H, 11.64). Quantitative reduction in acetic acid using Adams catalyst required 102% of two molar equivalents of hydrogen. Hydration with sulfuric acid and mercuric sulfate in acetic acid gave cyclononanone, identified as its semicarbazone (m.p. 179–180°). Mixed melting point with an authentic specimen showed no depression. Infrared spectrum of cyclononyne (Fig. 1) showed characteristic absorption for C≡C at 4.54 μ.

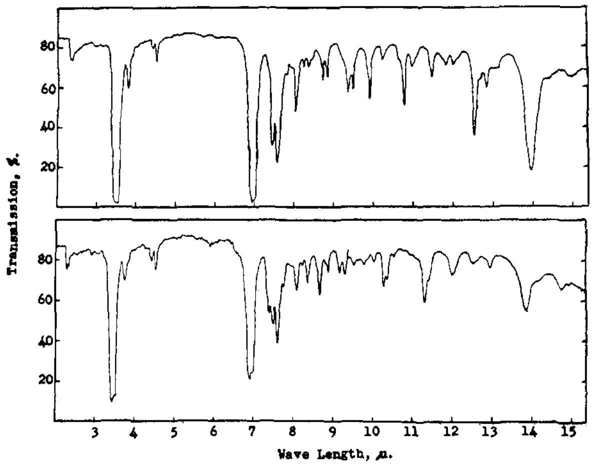


Fig. 1.—Upper curve infrared spectrum of cyclodecyne; lower curve infrared spectrum of cyclononyne.

Further details concerning these two cyclic acetylenes and the related cyclic *cis*- and *trans*-olefins will be presented as soon as possible in regular articles.

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RECEIVED SEPTEMBER 14, 1951

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## A NEW TOTAL SYNTHESIS OF ESTRONE

*Sir:*

We wish to announce a novel and relatively short total synthesis of estrone in which the rings are formed in the sequence A, C, B, D starting from anisole (as ring A).[1] The scheme is stereospecific, except for one step which at the present stage of development, nevertheless, proceeds so as to give the correct stereoisomer as the only crystallizable product in 36% yield.

The tribasic acid I (R = H) was produced as previously described,[2] by reduction of the product

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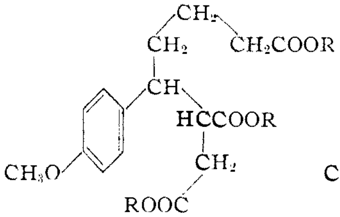
[3] N. A. Domnin, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 851 (1938); *Chem. Abs.*, **33**, 1282 (1939).

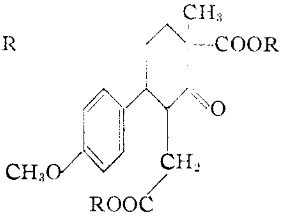
[4] T. Curtius, *Ber.*, **22**, 2161 (1889); T. Curtius and K. Thun, *J. prakt. Chem.*, [2] **44**, 168 (1891).

[1] This method was conceived prior to 1946 as an alternative to the approach of Johnson, Jones and Schneider (ref. 2); see also the M.S. thesis of W. P. Schneider, University of Wisconsin, 1946. A similar approach has been suggested independently by J. Dutta and D. K. Banerjee, *Science and Culture*, **12**, 408 (1947).

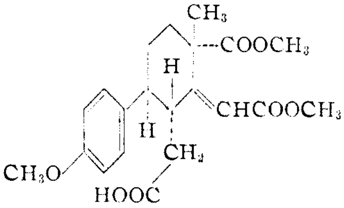
[2] W. S. Johnson, A. R. Jones and W. P. Schneider, THIS JOURNAL, **72**, 2395 (1950); see also D. L. Turner, *ibid.*, **73**, 1284 (1951).



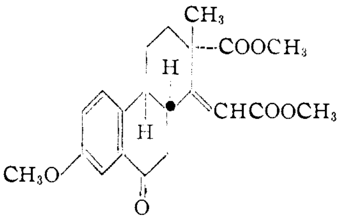
I



II



III



IV

from the Stobbe condensation of diethyl succinate with ethyl γ-anisoylbutyrate (prepared *via* the Friedel–Crafts reaction of glutaric anhydride with anisole). Dieckmann cyclization of the trimethyl ester I ($R = CH_3$) and methylation *in situ* gave the keto diester II ($R = CH_3$), m.p. 95–95.5°, which was crystallized directly from the reaction mixture in 36% yield.

Reformatsky reaction of II ($R = CH_3$) with methyl bromoacetate gave a mixture of a lactone (m.p. 112.5–113°; *Anal.* Calcd. for $C_{21}H_{26}O_7$: C, 64.60; H, 6.71. Found: C, 64.67; H, 6.75) and hydroxy ester (m.p. 101.2–101.9°; *Anal.* Calcd. for $C_{22}H_{30}O_8$: C, 62.54; H, 7.16. Found: C, 62.63; H, 7.27), which was not separated but treated directly with formic acid (to lactonize the hydroxy ester) followed by dilute sodium hydroxide which converted the mixture of isomeric lactones into essentially one form of the unsaturated mono acid III, m.p. 121–122°; *Anal.* Calcd. for $C_{21}H_{26}O_7$: C, 64.60; H, 6.71. Found: C, 64.92; H, 6.78. Cyclization of III by the inverse Friedel–Crafts method[3] gave a single keto diester IV, m.p. 147.8–148.4°; *Anal.* Calcd. for $C_{21}H_{24}O_6$: C, 67.72; H, 6.50. Found: C, 68.02; H, 6.94. Hydrogenolysis of the keto group over palladium catalyst promoted by perchloric acid[4] yielded a single unsaturated diester IV (methylene in place of keto group), m.p. 112–112.2° (perhaps the same as Anner and Miescher's[5] isomer m.p. 113–115°), which on further hydrogenation in neutral medium gave practically exclusively, racemic dimethyl marrianolate methyl ether, m.p. 99.5–100° (reported,[5] 95–96°). At this stage all four of the asymmetric centers have been introduced, and the subsequent steps involve no stereochemical problems. Partial saponification and homologation by the Arndt–Eistert reaction afforded, as previously described,[5] homomarrianolic acid methyl ether, m.p. 224.2–225.8°, undepressed on admixture with authentic material.[6] Cyclization of the dibasic acid yielded *dl*-estrone methyl ether, m.p. 143.2–144.2°, undepressed on admixture with an authentic specimen.[6] The demethylation and resolution of this product have already been described.[5,6]

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[3] W. S. Johnson and H. J. Glenn, THIS JOURNAL, **71**, 1092 (1949).

[4] The method of Kindler; see K. W. Rosenmund and E. Karg, *Ber.*, **75**, 1850 (1942).

[5] G. Anner and K. Miescher, *Helv. Chim. Acta*, **31**, 2173 (1948).

[6] W. S. Johnson, D. K. Banerjee, W. P. Schneider and C. D. Gutsche, THIS JOURNAL, **72**, 1426 (1950).

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RECEIVED AUGUST 7, 1951

## VARIATION OF ELECTRIC DIPOLE MOMENT WITH BOND LENGTH

*Sir:*

A quantity of importance for the understanding of absorption intensities in the infrared is $\epsilon$, the derivative of the electric dipole moment of a bond with respect to the bond length, evaluated at the equilibrium internuclear distance.[1] Bartholomé[2] has estimated $\epsilon$ for HCl, HBr and HI from absorption intensities; experimental difficulties make the values thus obtained somewhat uncertain.

Recently a new point of view as to the origin of electric dipole moments in molecules has been published.[3] It seems worth while to consider the variation of electric dipole moment with internuclear distance from the new point of view. According to equation (9) of the paper just mentioned, with accompanying discussion, a bond moment may be considered as arising from an internal field, $E$, of the form

$$E = e\left[\frac{Z_a}{R_a^2} - \frac{Z_b}{R_b^2}\right] \qquad (1)$$

where the symbols have the same significance as previously. The bond moment is then given by the product of this field and the longitudinal polarizability, $b_l$, so that

$$\epsilon = \frac{du}{dR} = b_l\frac{dE}{dR} + E\frac{db_l}{dR} \qquad (2)$$

Consider first

$$\frac{dE}{dR} = e\frac{d}{dR}\left(\frac{Z_a}{R_a^2}\right) - e\frac{d}{dR}\left(\frac{Z_b}{R_b^2}\right) \qquad (3)$$

This term we claim to be effectively zero or negligible compared to the other term composing $\epsilon$; the reason for this is as follows. As was pointed out in the previous paper,[3] the quantity $E$ is a small difference of two large quantities. Neglecting this small difference, we find

$$Z_a/R_a^2 \approx Z_b/R_b^2 \qquad (4)$$

for two atoms $a$ and $b$; hence $Z/R^2$ must be approximately the same for different atoms. It therefore seems reasonable to assume that this quantity is approximately constant for the *same* atom when a

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[1] L. Pauling and E. B. Wilson, Jr., "Introduction to Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, pp. 309–310.

[2] E. Bartholomé, *Z. physik. Chem.*, **B23**, 131 (1933).

[3] R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, THIS JOURNAL, **73**, 2263 (1951).