Ring Closure of Ylidenemalononitriles. II. Steric Effects of a Ring at the β-Position

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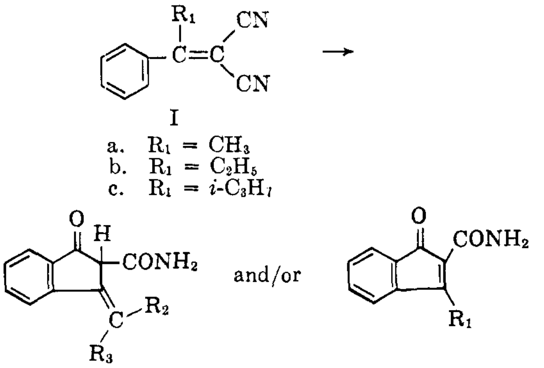
Heating 1-indanylidenemalononitrile (IVa) in concentrated sulfuric or polyphosphoric acid yielded the cyanoamide V. Using similar conditions, ring closure of 1-benzosuberylidenemalononitrile (IVc) to the tricyclic 2-carboxamidoindanone VII ($m = 3$) was effected. Structural assignment on the basis of the infrared and ultraviolet spectra of IVc, VII and related compounds is given.

Of special significance in the ring closure of α-cyano-β-substituted cinnamonitriles I were the steric influence of the groups in the β-position and the location of the olefinic bond after ring closure. It has been shown that both substituted indanones II and indenones III are produced when the ylidenemalononitriles Ib and Ic are treated with either concentrated sulfuric or polyphosphoric acid.[2] However, only the indenone VI ($n = 3$) was isolated when IVb, which is structurally similar to I, was cyclized.[2] Since the colorless indanones II were found to be the preferred structures for the ring-closed products,[2] it was surprising that when R_1 of structure I was part of a fused ring system, as in IVb, the colored indenone structure VI ($n = 3$) became the major isolated product. It was therefore interesting to examine the products of ring closure of other ylidenemalononitriles derived from cyclic benzo ketones IV to determine the steric effects of variation in the number of carbons (n) in the ring on the ring closure reaction, and on the nature of the product. The results of strong acid treatment of IVa and IVc, in which the saturated ring is one carbon less or one carbon more than in IVb,[3] are now reported.



I

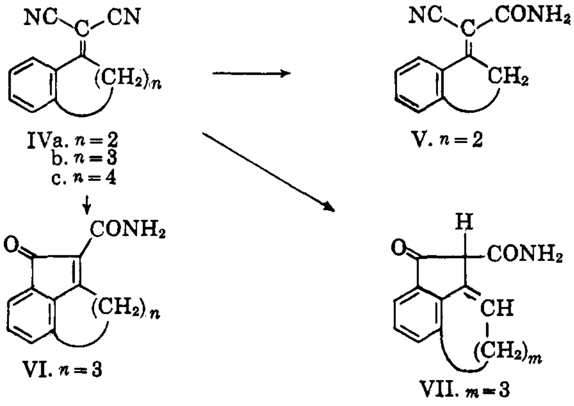
a. $R_1 = CH_3$
b. $R_1 = C_2H_5$
c. $R_1 = i\text{-}C_3H_7$

II

b. $R_2 = H, R_3 = CH_3$
c. $R_2 = R_3 = CH_3$

III

a. $R_1 = CH_3$
b. $R_1 = C_2H_5$
c. $R_1 = i\text{-}C_3H_7$



IVa. $n = 2$
b. $n = 3$
c. $n = 4$

V. $n = 2$

VI. $n = 3$

VII. $m = 3$

Only 1-indanylidenecyanoacetamide (V, $n = 2$) was formed when IVa was heated in concentrated sulfuric or polyphosphoric acid, while IVb and IVc did cyclize. The difficulty in cyclization of IVa can be attributed to its stereochemistry. The coplanarity of the molecule would permit deactivation of the aromatic ring to electrophilic attack by conjugated resonance with the protonated nitrile. In IVb and IVc, distortion of the resonance system by the skewed six- or seven-membered ring would interrupt conjugation and therefore ring closure (electrophilic attack by the $-\overset{+}{C}{=}NH$ group) would be facilitated. Furthermore, the ring closure of IVa would furnish a strained tricyclic 6,5,5-ring system, whereas ring closure of IVb furnishes a more stable 6,6,5-system, and IVc a 7,6,5-system.

Isolation of the indanone VII ($m = 3$) as the only cyclized product from 1-benzosuberylidenemalononitrile (IVc) appears as a somewhat surprising result, in view of the fact that ring closure of IVb gave only the indenone VI ($n = 3$) and none of the indanone VII ($m = 2$). That the olefinic bond in IVc was exocyclic and not endocyclic to the seven-membered ring before ring closure is indicated by its ultraviolet spectrum. Listed in Table I are the ultraviolet data for IV (a, b and c) and the α-cyano-β-substituted cinnamonitriles I (R=H, CH_3, C_2H_5, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$). As was earlier reported for the α-cyano-β-substituted cinnamonitriles,[2] the λ_{max} values (in the 282–313-mμ region) and the corresponding ε values systematically decrease as the β-alkyl group increases. However, in the 224–237-mμ region each log ε increases as the steric hindrance becomes greater. The peaks at 297 mμ ($\log \epsilon = 3.98$) and 231 mμ ($\log \epsilon = 4.0$) for IVc, in good agreement with those obtained from the other ylidenemalonitriles in Table I, are consistent with an exocyclic double bond, and furthermore show the degree of steric hindrance caused by the methylene groups, relative to the other ylidenemalononitriles. An α,β-unsaturated nitrile is also indicated by the infrared absorption peak at 2217 cm.$^{-1}$.[4] This is consistent with the $-C{\equiv}N$ stretching vibrational peak for a cyano group conjugated to a

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[1] Taken in part from a thesis submitted to Indiana University in partial fulfillment of the requirements for Ph.D. degree, June 1962, by D. R. Maulding, Bristol Predoctoral Fellow, 1960–1962.

[2] E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and Donald R. Maulding, *J. Org. Chem.*, **27**, 4428 (1962).

[3] E. Campaigne and G. F. Bulbenko, *ibid.*, **26**, 4703 (1961).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 263.

TABLE I

ULTRAVIOLET SPECTRA OF YLIDENEMALONONITRILES[a]

Compound	$\lambda_{\max}$, mμ	log ϵ	Other Peaks $\lambda_{\max}$, mμ	Other Peaks log ϵ
I (R = H)	309	4.31	231	3.89
			224	3.92
Ia	292	4.11	232	3.88
			228	3.86
Ib	292	4.11	232	3.92
			229	3.91
Ic	283	3.73	232	4.04
I (R = t-C_4H_9)	282	2.79	236	4.31
IVa	308	4.18	237	3.91
			230	3.97
IVb	313	4.12	237	3.75
			231	3.76
IVc	297	3.98	231	4.00

[a] The ultraviolet absorption spectra were determined in 95% ethanol with a Cary Model 14 ultraviolet recording spectrophotometer.

double bond found for compounds I (R = H), Ia, Ib, Ic, I (R = t-C_4H_9), IVa, IVb and IVc.

The infrared spectrum, elemental analysis and molecular weight determination substantiate the structural assignment of the cyclized product from IVc as VII ($m=3$). Besides the two NH stretching absorptions at 3410 cm.$^{-1}$ and 3185 cm.$^{-1}$, characteristic of a primary amide, the infrared spectrum of VII ($m=3$) also contained a ketonic CO peak at 1712 cm.$^{-1}$. The latter peak, as well as the carbonyl stretching vibrations for IIb, IIc (1715 cm.$^{-1}$ and 1720 cm.$^{-1}$) are significantly shifted to lower wave lengths when compared to the indenones, IIIa, IIIb, IIIc and VI ($n=3$), which have peaks at 1705 (broad), 1702, 1698 and 1696 cm.$^{-1}$, respectively. Also, the fact that VII ($m=3$) is white and not colored supports the probability of an indanone and not an indenone.[2] Further evidence for this structure is offered by the ultraviolet spectrum, which has a peak at 246 mμ (log ϵ = 4.13). This single, sharp peak in the 240–250-mμ region is indicative of an indeanone and not an indenone, since IIb and IIc have absorptions at 239 mμ (log ϵ = 4.50) and 242 mμ (log ϵ = 4.54). In comparison, the 2-carbamoyl-3-alkyl-1-indenones, IIIa, IIIb and IIIc have distinct doublets at 247 mμ (log ϵ = 4.62) and 252 mμ (log ϵ = 4.61), 244 mμ (log ϵ = 4.56) and 249 mμ (log ϵ = 4.55), 247 mμ (log ϵ = 4.56) and 252 mμ (log ϵ = 4.53). It should be noted that the ketoamide VI ($n=3$) also has a doublet at 252 mμ (log ϵ = 4.60) and 259 mμ (log ϵ = 4.59).

In conclusion, the close similarity of the ultraviolet spectra of IVa and benzylidenemalononitrile (Table I) and the fact that neither of these compounds yield ring-closed products in concentrated acid, may indicate a similar planar unstrained structure. Furthermore, the fact that the indenone ($n=3$) is the preferred structure of the cyclized product from IVb, while the indanones are the preferred products from Ib, Ic and IVc, indicates a degree of strain in the 6,6,5-fused system not found in the 7,6,5-fused system nor in the simple indanones, II.

Experimental

All melting points reported are corrected. The microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana. The infrared spectra were recorded by a Perkin–Elmer 137-G grating spectrometer. All ultraviolet spectra were determined in 95% ethanol with a Cary Model-14 recording spectrophotometer.

Preparation of Benzosuberone.—Starting with freshly distilled cinnamaldehyde, cinnamylidenemalonic acid was prepared in 43% yield according to the procedure described by Baker and Aspinall,[5] by condensation with ethyl malonate and subsequent alkaline hydrolysis. Following the method reported by Cook, Phillip and Somerville,[6] the unsaturated acid was reduced with Raney nickel and decarboxylated. The resulting δ-phenylvaleric acid, obtained in 83% yield, was cyclized in polyphosphoric acid[7] to produce benzosuberone in 79% yield. The over-all yield from cinnamaldehyde in this sequence was 28%.

1-Indanylidenemalononitrile (IVa).—1-Indanone (13.2 g., 0.10 mole), prepared by the method of Snyder and Weber,[8] 7.9 g. (0.12 mole) of malononitrile, 1.6 g. of anhydrous ammonium acetate, and 4.8 ml. of glacial acetic acid were refluxed in 100 ml. of anhydrous benzene for 6 hours, using a Dean-Stark moisture trap. White crystals were obtained after the benzene solution was washed with water, dried with sodium sulfate and evaporated. Recrystallization from ethanol yielded 7.3 g., 40%, of white needles, m.p. 154–155°[9]; $\nu_{\max}^{\mathrm{KBr}}$ 2220 cm.$^{-1}$ (CN); ultraviolet spectral data, see Table I.

Anal. Calcd. for $C_{12}H_8N_2$: N, 15.55. Found: N, 15.42.

1-Benzosuberylidenemalononitrile (IVc).—Eight grams of benzosuberone, 4 g. of malononitrile, 0.4 g. of anhydrous ammonium acetate and 1.5 ml. of glacial acetic acid were refluxed in 100 ml. of anhydrous benzene for 8 hr. using a Dean–Stark trap. The benzene solution was washed with water, dried with sodium sulfate and evaporated. Distillation of the resulting oil under reduced pressure yielded 2 g. of starting ketone and a second fraction, b.p. 135–142°/0.25 mm., which became crystalline upon standing. Recrystallization from aqueous ethanol gave 4.8 g. of white flakes, m.p. 76–77°; $\nu_{\max}^{\mathrm{KBr}}$ 2217 cm.$^{-1}$; ultraviolet spectral data, see Table I.

Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.77; H, 5.77; N, 13.46. Found: C, 80.39; H, 5.95; N, 13.22.

Attempted Cyclization of 1-Indanylidenemalononitrile (IVa.)—A brown color developed when 2 g. of IVa was dissolved in 30 ml. of concentrated sulfuric acid and maintained at 50–55° for 2 hr. Pouring the acid solution into 200 g. of ice caused the precipitation of a white solid and recrystallizing from ethanol gave 1.9 g., 86%, of V ($n=2$), m.p. 197–198°; $\nu_{\max}^{\mathrm{KBr}}$ 3480 (free NH), 3205 (H-bonded NH), 2230 (CN) and 1665 cm.$^{-1}$ (amide CO). A much lower yield (12%) of V ($n=2$) was obtained by heating 2 g. of IVa in 30 ml. of concentrated sulfuric acid on a steam bath for 15 min. The yield of V ($n=2$) when 2 g. of IVa was heated in 40 g. of polyphosphoric acid on a steam bath for 2 hr. then poured into 400 g. of ice, was 1.2 g. or 56%.

Ring Closure of 1-Benzosuberylidenemalononitrile (IVc).—One and one-half grams of IVc was heated at 55–60° in 15 ml. of concentrated sulfuric acid for 2 hr. The hot, dark red solution was poured into 120 g. of ice. Recrystallization of the precipitated yellow solid from ethanol gave 1.27 g., 77%, of white prisms, m.p. 188–189°; $\nu_{\max}^{\mathrm{KBr}}$, 3410 (free NH), 3185 (H-bonded NH), 1712 (CO) and 1635 cm.$^{-1}$ (amide CO); $\lambda_{\max}$, 246 mμ (log ϵ = 4.13), broad shoulder at 255–277 mμ (log ϵ = 3.96 − log ϵ = 3.81), 337 mμ (log ϵ = 2.92). The yields of VII ($m=3$) were 56% and 60% when the same quantities of IVc were heated in concentrated sulfuric acid on a steam bath for 15 min. or in polyphosphoric acid (20 g. of acid per 1 g. of dinitrile) for 5 hr.

Anal. Calcd. for $C_{14}H_{13}NO_2$: C, 74.01; H, 5.72; N, 6.17; mol. wt. 227. Found: C, 73.91; H, 5.86; N, 6.15; mol. wt. 224 (determined in chloroform on a Mechrolab vapor pressure osmometer Model 301A).

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[8] H. R. Snyder and F. X. Weber, *ibid.*, **72**, 2965 (1950).

[9] D. M. W. Anderson, F. Bell, and J. L. Duncan, *J. Chem. Soc.*, 4705 (1961), reported a melting point of 152°.