752, 740, 733, 706 cm^{-1}; UV (isooctane) λ_{max} 234.5 (sh), 285.5, 293.5 (ϵ 10 010, 640, 530); ^1H NMR (CCl_4) δ 1.60–2.30 (m, 4 H), 2.52–3.28 (m, 8 H), 5.32 (d, 2 H), 6.78, 6.79 (AB quartet, J_{ab} = 8 Hz, 4 H); ^{13}C NMR ($CDCl_3$)[19] δ 35.4, 35.7, 37.4, 127.8, 129.1, 134.5, 139.3, 139.4, 139.5; MS *m/e* 234 (M^+).

Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.80.

Registry No.—**2**, 58002-98-5; **6**, 63877-75-8; **7**, 64884,24,8; **8**, 38460-57-0; **9**, 61124-37-6; **10**, 63877-74-7; **11**, 64316-88-7; **12**, 64924-60-3; **13**, 64884-26-0; **14**, 64884-27-1; **15**, 64976-19-8; **16**, 64924-60-3; 1,2,4-tricarbomethoxybenzene, 2459-10-1; 1,2,4-tris(hydroxymethyl)benzene, 25147-76-7; phosphorus tribromide, 7789-60-8; thiourea, 62-56-6.

References and Notes

(1) Presented in part at the 36th Annual Meeting of the Chemical Society of Japan, Osaka, Japan, April 1, 1977, abstracts II, p 580, and a preliminary report of the synthesis of [2.2.2](1,2,4)(1,3,5)cyclophane has been published: M. Nakazaki, K. Yamamoto, and Y. Miura, *J. Chem. Soc., Chem. Commun.*, 206 (1977).
(2) The nomenclature used is that proposed by F. Vögtle and P. Neumann, *Tetrahedron*, **26**, 5847 (1970).
(3) V. Boekelheide and R. A. Hollins, *J. Am. Chem. Soc.*, **93**, 3512 (1970); *ibid.*, **95**, 3201 (1973).
(4) D. J. Cram and E. A. Truesdale, *J. Am. Chem. Soc.*, **95**, 5825 (1973).
(5) V. Boekelheide and R. Gray, *Angew. Chem. Int. Ed. Engl.*, **14**, 107 (1975).
(6) W. Gilb, K. Menke, and H. Hopf, *Angew. Chem., Int. Ed. Engl.*, **16**, 191 (1977).
(7) M. Nakazaki, K. Naemura, and H. Yoshihara, *Bull. Chem. Soc. Jpn.*, **48**, 3278 (1975).
(8) M. Nakazaki, "Syntheses and Stereochemistry of Twisted Organic Compounds", Invited Lecture at 30th National Meeting of the Chemical Society of Japan, Osaka, April 1974, abstracts V, p 1.
(9) M. Nakazaki, K. Yamamoto, and M. Itoh, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki and K. Yamamoto, *Chem. Lett.*, 1051 (1974).
(10) M. Nakazaki, K. Yamamoto, and S. Tanaka, *J. Chem. Soc., Chem. Commun.*, 433 (1972); M. Nakazaki, K. Yamamoto, S. Tanaka, and H. Kametani, *J. Org. Chem.*, **42**, 287 (1977).
(11) M. Nakazaki, K. Yamamoto, and J. Yanagi, *J. Chem. Soc., Chem. Commun.*, 346 (1977); J. A. Marshall and M. Lewellyn, *J. Am. Chem. Soc.*, **99**, 3508 (1977).
(12) H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3505, 3527 (1969).
(13) F. Vögtle, *Justus Liebigs Ann. Chem.*, **735**, 193 (1970).
(14) The structural formula of **6, 7, 10, 15, 17,** and **18,** respectively, represent one of their possible enantiomers.
(15) Vögtle has shown that the condensation of 1,3,5-tris(bromomethyl)benzene with 1,3,5-tris(mercaptomethyl)benzene (**8**) proceeded with only 5.3% yield.[13]
(16) J. Bruhin and W. Jenny, *Tetrahedron Lett.*, 1215 (1973); V. Boekelheide, I. D. Reingold, and M. Tuttle, *J. Chem. Soc., Chem. Commun.*, 406 (1973).
(17) M. Haenel and H. A. Staab, *Tetrahedron Lett.*, 3585 (1970); *Chem. Ber.*, **106**, 2190 (1973).
(18) [2.2.2](1,3,5)Cyclophane (**1**) has been reported to be prepared by pyrolysis of the corresponding trisulfone in a 20% yield.[3]
(19) Chemical shifts are expressed in parts per million relative to Me_4Si.
(20) The heavily shielded proton in [2.2]metaparacyclophane is exhibited at δ 5.24; D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Am. Chem. Soc.*, **88**, 1324 (1966).
(21) 1,2,4-Tricarbomethoxybenzene, bp 171–173 °C (0.1mm), was prepared by the esterification of 1,2,4-benzenetricarboxylic acid with methanol containing sulfuric acid.

Rearrangement of 2-Cyano-3-(1-methylcyclopentyl)indenone to 4a-Methyl-9-oxo-10-cyano-1,2,3,4,4a,9-hexahydrophenanthrene[1a]

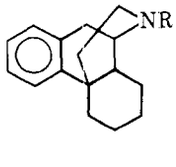
E. Campaigne* and Ronald A. Forsch[1b]

Department of Chemistry, Indiana University, Bloomington, Indiana 47401

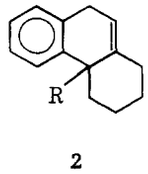
Received August 19, 1977

The possibility of preparing partially saturated phenanthrenes with 2-aminoethyl side chains at the 4a position, key precursors in the synthesis of the pharmacologically important morphinan ring system, by a complex carbonium ion rearrangement of the title compounds was explored. Thus, treatment of 1-methylcyclopentanecarbonitrile (**1**) with phenyllithium followed by malononitrile quench gave α-cyano-β-(1-methylcyclopentyl)cinnamonitrile (**2**), which on treatment with sulfuric acid gave a low yield of 3-(1-methylcyclopentyl)-2-cyanoindenone (**3**). Treatment of **3** with sulfuric acid gave 4a-methyl-9-oxo-10-cyano-1,2,3,4,4a,9-hexahydrophenanthrene (**4**) by a rearrangement involving migration of a cyclopentyl carbon followed by a phenyl migration. The structure expected by the reverse sequence of migrations, 2′-methyl-3′-cyanospiro[cyclopentane-1,1′(4′*H*)-naphthalene]-4′-one (**5**), was eliminated as a possible structure of the product by unambiguous synthesis of its Michael cyanide adduct **6** from a known compound (the parent enone of **5**) and comparison of **6** with the Michael cyanide adduct of **4**, with which it was not identical. Attempted cyclization of compounds analogous to **2** with side chains larger than methyl (methoxymethyl, phenyl, and benzyl) was not successful.

The morphinan ring system (**1**) is contained in a number of drugs being studied for use as narcotic antagonists or nonaddictive analgetics. The synthesis of this ring system from partially saturated phenanthrenes with an angular side chain such as **2** (R = $CH_2CH_2NH_2$) has now been studied in some detail.[2–6] The known rearrangement of 3-*tert*-butyl-2-cyanoindenone to give 2-cyano-3,4,4-trimethyl-1-oxo-1,4-dihydronaphthalene,[7] which has a quaternary carbon atom, suggested the possibility of preparing compounds of type **2**



1



2

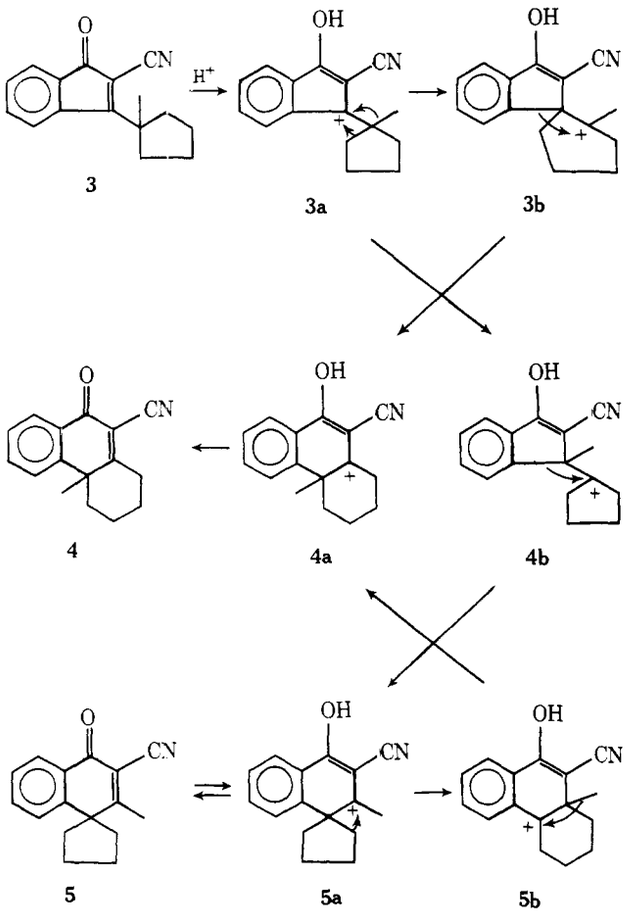
by carbonium ion rearrangement of suitably substituted indenones.[8a]

The use of ylidenemalononitriles as precursors to indenones has recently been reviewed.[8a] An example[7] is the cyclization of pivalophenylidenemalononitrile to 2-cyano-3-*tert*-butylindenone, which probably involves as an intermediate an iminium species, the stability of which prevents further acid rearrangement. The ylidenes may be prepared from ketones by condensation with malononitrile, or, alternatively, by malononitrile quench of the imine salts formed by the addition of organometallic reagents to nitriles, e.g., phenyl Grignard to pivalonitrile. The latter method is especially advantageous when the required ketone would be hindered.[8b]

If two of the methyl groups of the *tert*-butyl group were linked by a two-carbon bridge, as in **3** (Scheme I), the reaction would be a possible example of a double ring expansion approach to the phenanthrene ring system. The tertiary carbo-

0022-3263/78/1943-1044$01.00/0

Scheme I



nium ion **3a** would be expected to undergo ring enlargement to a second tertiary carbonium ion **3b**. A second ring enlargement involving a phenyl migration would produce the protonated hydrophenanthrene structure **4a**, which by loss of a proton would give 4a-methyl-9-oxo-10-cyano-1,2,3,4,4a,9-hexahydrophenanthrene (**4**). An alternative rearrangement of **3** involving migration of the methyl group in preference to a ring carbon to give the spiro compound **5** may also be possible (Scheme I). In this case, methyl migration in carbonium ion **3a** followed by ring enlargement of the resulting carbonium ion **4b** would lead to the spiro carbonium ion **5a**, which could lose a porton to produce 2′-methyl-3′-cyanospiro[cyclopentane-1,1′(4′*H*)-naphthalen]-4′-one (**5**). Alternatively, **5a** could undergo ring enlargement to the protonated hydrophenanthrene **5b**, which by methyl migration would ultimately give the desired product **4**. Thus, compound **4** could theoretically arise by either path. However, the rearrangements **3a** → **4b** → **5** shown in Scheme I would not be expected since it is known[9] that α-methylcyclopentyl phenyl ketone rearranges quantitatively in concentrated perchloric acid to give 2-methyl-2-phenylcyclohexanone, the product arising from initial migration of a ring carbon rather than the methyl group. The rearrangement substrate **3** in Scheme I is a vinylogue of α-methylcyclopentyl phenyl ketone.

Compound **3** was prepared from 1-methylcyclopentanecarbonitrile. A recent method[10] for the preparation of 1-substituted compounds of this type using a primary nitrile, 1-chloro-4-bromobutane as the alkylating agent, and lithium diethylamide as the base in hexamethylphosphoramide was rejected due to the high cost of the alkylating agent. An earlier paper[11] describing a similar reaction with the economical 1,4-dibromobutane and sodamide reported low yields. We found that good yields of 1-methylcyclopentanecarbonitrile could be obtained by treating propionitrile with 1,4-dibromobutane and lithium diisopropylamide in tetrahydrofuran, provided the reaction was carried out at low temperatures. The structure was supported by infrared, NMR, and mass spectra, but the compound was not obtained in analytically pure form owing to traces of halide which tended to codistill. Attempted hydration[12] to the corresponding amide was not successful.

Table I. Comparison of Chemical and Physical Data of Rearrangement Substrate 3 with Product 4 and 2-Cyano-3,4,4-trimethyl-1-oxo-1,4-dihydronaphthalene

Compd	3	4	Model compd[a]
Color	Bright yellow	White	White
Mp, °C	137–138	90–91	164–165
MW (*m/e*)	237	237	
IR (KBr), μm			
C=O	5.85	6.07	6.02[b]
CN	4.54	4.51	4.44[c]
NMR, δ			
Me	1.57	1.53	1.61, 2.50
$(CH_2)_4$	1.0–3.0	1.7–2.6	
Anal. Calcd for $C_{16}H_{15}NO$:	Found:	Found:	
C, 80.98	81.04	80.88	*d*
H, 6.37	6.09	6.57	
N, 5.90	6.15	6.19	

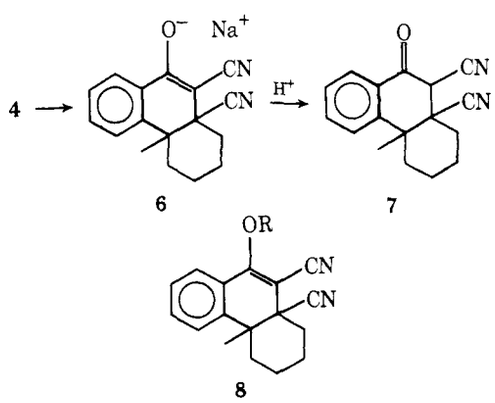
[a] E. Campaigne and D. Maulding, *J. Org. Chem.*, **28**, 1391 (1963). [b] Calculated from the published value of 1662 cm^{-1}. [c] Calculated from the published value of 2250 cm^{-1}. [d] Satisfactory elemental analyses (within 0.3%) were obtained.

Treatment of 1-methylcyclopentanecarbonitrile with phenyllithium and malononitrile[8b] gave α-cyano-β-(1-methylcyclopentyl)cinnamonitrile, which on treatment with concentrated sulfuric acid cyclized in low yield to give the target indenone **3**. The remainder of the product mixture was water-soluble sulfonated material.[13]

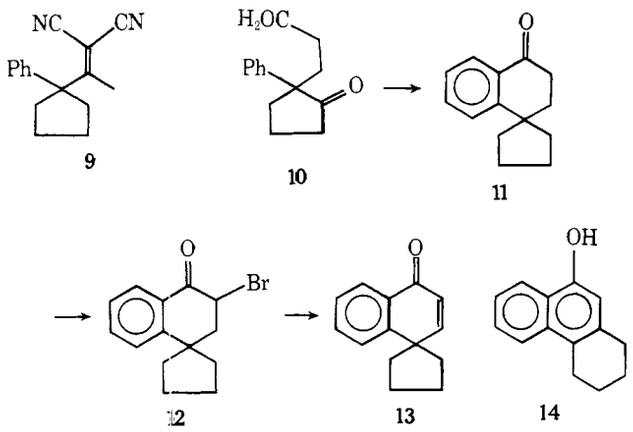
The rearrangement was carried out in good yield by treating the indenone **3** with concentrated sulfuric acid.[7] Comparison of the infrared and NMR spectra of the product with the spectra of 2-cyano-3,4,4-trimethyl-1-oxo-1,4-dihydronaphthalene suggested that it was the desired hexahydrophenanthrene **4**. The substrate, product, and model compound are compared in Table I.

Compound **4** was further characterized by conversion to derivatives.. These reactions are outlined in Scheme II. Treatment of **4** with sodium cyanide in aqueous *tert*-butyl alcohol gave a product which on dilution with water remained in the aqueous layer even after extraction with ether, suggesting it to be the salt **6**. Acidification gave the dinitrile **7** in equilibrium (about 1:1 by NMR in deuteriochloroform) with its enol **8** (R = H). Kulp et al.[14] have previously reported

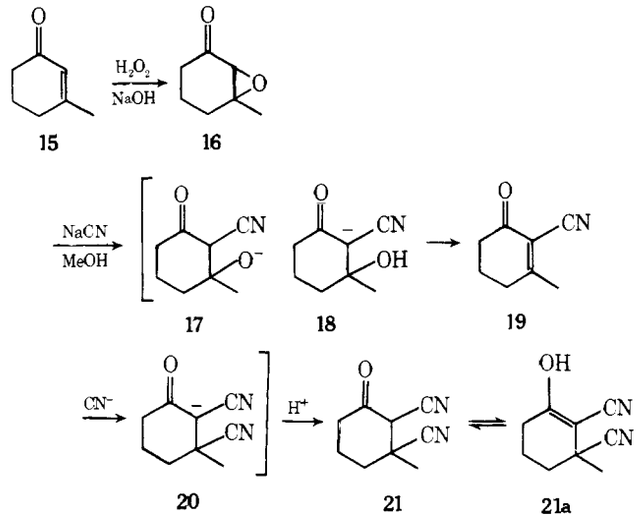
Scheme II



Scheme III



Scheme IV



similar keto–enol equilibria in 2-cyanocyclohexanones, but only 6,6-disubstituted cases were included in that study. The product is surprisingly acidic, being readily soluble in 5% aqueous sodium bicarbonate with gentle warming. The enol ether **8** (R = CH_3) was prepared by treating **7** with potassium *tert*-butoxide and methyl iodide. Attempted condensation of **7** with hydrazine resulted in retro-Michael loss of hydrogen cyanide to regenerate the enone **4** in low yield amid a complex mixture of products. An attempted alternate synthesis of **4** by cyclization of the known[15] 2-methyl-2-phenylcyclohexylidenemalononitrile failed.

Although the structure of the acid rearrangement product of **3** was confirmed by spectra and properties of derivatives as **4**, it was desirable to compare the properties of **4** with its isomer **5**, an unambiguous synthesis of which was needed. An obvious approach, the cyclization of the ylidenemalononitrile **9** (Scheme III), was unsuccessful. This is in marked contrast to the behavior of the analogous compound with two methyl groups instead of a cyclopentane ring, which was successfully converted to the ketone.[7] The required ylidene **9** was made by the usual route[8b] from 1-phenylcyclopentanecarbonitrile, which in turn is available by dialkylation of phenylacetonitrile using a two-phase system.[16]

Arnold and co-workers[17] purportedly prepared the enone **13** (Scheme III) as a substrate for the dienone–phenol rearrangement, which under the conditions of the reaction gave the acetate of **14** as the product. Curiously, they did not characterize **13** at all except to obtain an elemental analysis of an oil.

This work was duplicated without difficulty up to the preparation of the bromo ketone **12**, but in our hands the enone **13** always rearranged sometime before distillation could be completed, usually observable by the sudden generation of intense heat in the receiving flask and conversion of the distillate to **14**. This sudden reaction is probably caused by decomposition of residual collidine hydrobromide, formed in the dehydrobromination of **12**, giving gaseous hydrogen bromide which is absorbed in the distillate, and shows the sensitivity of **13** to traces of acid. This problem was circumvented by carrying out the dehydrobromination of **12** by a more recently developed method[18] using a suspension of lithium carbonate and lithium bromide in dimethylformamide. When this was done, pure enone **13** could be isolated, and the yield was somewhat better. It is in fact a solid, mp 32–34 °C, showing carbonyl absorption in the infrared spectrum at 6.00 μm and giving vinyl hydrogen signals (doublet, J = 10 Hz) in the NMR spectrum at δ 6.19 and 6.90. Interestingly, all eight cyclopentyl hydrogens are equivalent, appearing as s sharp singlet (60 MHz) at δ 2.00.

The required starting material, 2-phenylcyclopentanone, was prepared by Arnold[17] from 2-chlorocyclopentanone and phenyl Grignard. A more recent method[19] involving performic acid oxidation of 1-phenylcyclopentene followed by heating was, however, more efficient and reliable.

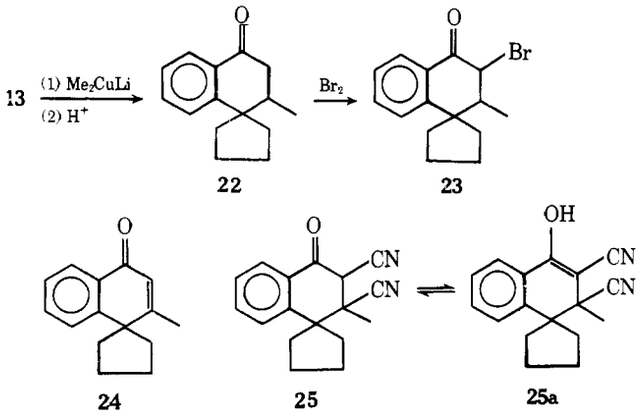
The conversion of **13** to **5** requires placement of a methyl group at the β position and a cyano group at the α position with retention of the double bond. Introduction of the methyl group at the β position by conjugate addition of lithium dimethyl copper to the enone **13** followed by regeneration of the double bond is feasible, but introduction of the cyano group at the α position seemed difficult. We therefore decided to use the enone **15** as a model substrate. Specifically, we were interested in determining whether epoxidation followed by cleavage of the epoxide ring by cyanide would lead to the keto nitrile **19** (Scheme IV).

Treatment of **15**[20] with alkaline hydrogen peroxide gave the known[21] epoxide **16**. When this epoxide was allowed to react with methanolic cyanide the product obtained (after acidification) was the dinitrile **21**, in equilibrium with its enol **21a**. The yield of this dinitrile approximately doubled if excess cyanide was used instead of 1 equiv. (Methanolysis is the competing reaction.) Thus, it is best to use at least 2 equiv of cyanide and convert all of the epoxide to dinitrile. These results can be rationalized (Scheme IV) by assuming initial reaction of cyanide at the 2 carbon to give the intermediate **17**, which undergoes proton transfer owing to the presence of the acidic hydrogen now between the carbonyl and cyano groups. This new intermediate (**18**) suffers retro-Michael loss of hydroxide to give the desired enone nitrile **19**. However, this compound, apparently an avid Michael acceptor, reacts with more cyanide ion to give **20**, which an acidification gives the product.

The dinitrile **21** is strongly acidic, being easily extractable into 5% aqueous sodium bicarbonate. Crystals obtained from benzene gave an infrared spectrum (potassium bromide) that showed mostly keto form present, but an NMR spectrum (deuteriochloroform and acetone-d_6) showed it to be about 70% enolized. There are two diastereoisomers of the ketone **21**. The NMR spectrum shows two broadened singlets, one at δ 4.00 and the other (about one-fourth as large) at δ 4.21, for a total of 0.3 hydrogen. We are unable to tell which signal arises from which isomer. Efforts to reverse the second cyanide addition by refluxing the dinitrile in the presence of acetic acid and triethylamine in alcohol were unsuccessful. Treatment with excess hydroxide followed by acidification was also unsuccessful. In both cases the starting material was recovered.

Treatment of **13** with lithium dimethyl copper gave the saturated methylated ketone **22** (Scheme V), which in a separate step was brominated to give **23**. Dehydrobromination

Scheme V



gave the methylated enone **24**, which, in contrast to **13**, was so stable to acid that it could be recovered unchanged after being dissolved in 96% sulfuric acid. This marked difference in behavior is no doubt due to the inability of **24** to aromatize by rearrangement and indicates the rearrangement of **5** to **4** (Scheme I) is unlikely. This result was not surprising since the 3,4,4-trimethyl enone is known to be stable to acid also.[22] By coincidence, all eleven alkyl hydrogens in **24** were equivalent in the NMR (60 MHz) spectrum.

The conversion of **24** to **25** is exactly analogous to the conversion of **15** to **21** (Scheme IV). The intermediate epoxide was not isolated, but infrared spectroscopy did show a shift in the carbonyl stretch from 6.07 μm in **24** to 5.93 μm, indicating that the olefinic bond had indeed reacted.

The spiro dinitrile **25** could then be compared to the compound believed to be the hydrophenanthrene dinitrile **7** obtained by Michael addition of cyanide to **4** (Scheme II). The fingerprint regions of the infrared spectra of the two compounds were quite different, although the functional group regions were nearly identical. Comparison of the properties of the two compounds (Table II) clearly shows their nonidentity. Owing to the presence of one enol tautomer and cis and trans forms of the keto tautomer, there are three different shifts observed for the methyl group in **25**. In acetone-d_6 the compound was more than 50% enolized (by NMR). Compound **7** shows a spike in the NMR spectrum at δ 1.58 of uncertain origin. There exists the possibility that both cis and trans forms of this compound are present also, but the spike is not quite as sharp as the main peak and may merely be an alkyl signal of the ring.

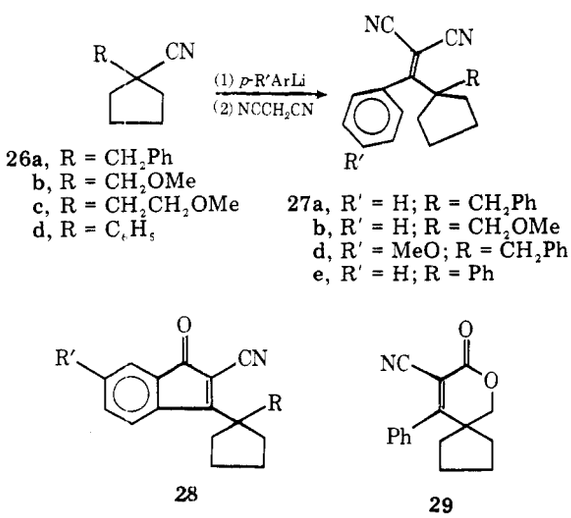
With the utility of an appropriately substituted indenone as a precursor to a hexahydrophenanthrene with an angular methyl group established, an attempt was made to extend this study to the preparation of compounds of structure **28** (Scheme VI), where the R group was larger than methyl. For such a study a variety of 1-substituted cyclopentanecarbonitriles (**26**) was required. These could most conveniently be made by alkylation of cyclopentanecarbonitrile itself.

Table II. Comparison of Chemical and Physical Data of 7 and 25

Compd	7	25
Color	White	White
MP,[a] °C	162.0–163.5	169–170
IR (KBr), μm		
C=O	5.91	5.89
CN	4.55	4.54
NMR (acetone-d_6), δ		
Me	1.71	1.52
	1.58 (spike)	1.55
		1.59
Alkyl	1.3–2.9	0.5–2.2
MW (*m/e*)	264	264
Anal. Calcd for $C_{17}H_{16}N_2O$:	Found:	Found:
C, 77.25	76.92	77.25
H, 6.10	6.03	6.15
N, 10.60	10.37	10.44

[a] The melting point of the mixture is depressed.

Scheme VI



Cyclopentanecarbonitrile has been prepared by treatment cyclopentyl chloride with cyanide[27] or by dialkylation of acetonitrile with 1,4-dibromobutane and sodamide.[28] The compound was most conveniently prepared from ethyl 1-cyanocyclopentanecarboxylate, readily available by ring annelation of ethyl cyanoacetate with 1,4-dibromobutane by treatment with sodium cyanide in hot dimethyl sulfoxide. This may involve attack of cyanide on the ester to produce a carboxylate salt, which could then decarboxylate to give the product after protonation. A similar type of reaction has been used[29] for conversion of β-keto esters to ketones. A method reported[30] for conversion of monosubstituted α-cyano esters to the corresponding nitriles using sodium chloride in wet dimethyl sulfoxide was unsuccessful here.

Alkylation of this nitrile with lithium diisopropylamide and benzyl chloride, methyl chloromethyl ether, or 2-methoxyethyl chloride in tetrahydrofuran (Scheme VI) gave the desired compounds **26** in moderate yield with recovery of unchanged nitrile accounting for the balance of starting material. Satisfactory elemental analyses were obtained for the new compounds **26b** and **26c**. Compound **26a** had been previously prepared[31] from 3-phenylpropionitrile and 1,4-dibromobutane in the presence of sodamide.

Treatment of **26a** and **26b** with aryllithium reagents followed by malononitrile quench gave the expected[8b] compounds **27** in good yields, but an analytically pure sample of **26c** failed to react with phenyllithium even under conditions more vigorous than those usually used, e.g., in refluxing tetrahydrofuran. Compound **27e** was prepared from the corresponding 1-phenylcyclopentanecarbonitrile, described earlier.

Cyclization of the compounds **27a–e** using all acid catalysts known to be effective in this reaction[8] failed in every case. The lactone **29** was obtained in low yield when **27b** was treated with acid. This lactone formation from an ether is formally similar to an acid cyclization observed with ylidenemalononitriles bearing an aromatic ether oxygen.[32]

Since we were unable to obtain indenones of type **28**, other than R = methyl, we have not been able to determine whether 4a-substituted hydrophenanthrenes, with groups other than methyl at the 4a position, can be obtained by this route.

Experimental Section

Melting points were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 infrared spectrometer. NMR spectra were obtained on a Varian Associates EM-360 instrument using tetramethylsilane as an internal standard. Magnesium sulfate was used as the drying agent except where otherwise indicated. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

2-Phenylcyclopentanone was prepared from 1-phenylcyclopentene[19] by treatment with performic acid[19] followed by heating. The yield was 46% as a colorless liquid which was unstable on prolonged storage, bp 105–107 °C (2.2 mm) [lit.[19] bp 115–116 °C (3 mm)].

1-Phenylcyclopentanecarbonitrile. Phenylacetonitrile (0.1 mol, 11.7 g) and 0.1 mol (12.7 g) of 1,4-dichlorobutane were stirred together with 0.5 g of benzyltriethylammonium chloride briefly. Then 30 mL of 50% sodium hydroxide was added, and the mixture was stirred vigorously at 80 °C overnight. After cooling, the mixture was diluted with water and extracted with ether, and the ether layer was washed with water and brine, dried, and evaporated. The residue was distilled to give 10.1 g (59%) of product as a colorless liquid, bp 110 °C (2 mm), in agreement with the literature[16] value.

Cyclopentanecarbonitrile. Ethyl 1-cyanocyclopentanecarboxylate was prepared by alkylating ethyl cyanoacetate, substituting 1,4-dibromobutane for 1,4-dichlorobutane (*Caution!* cooling) in the published procedure,[33] which permitted a decrease in the reaction time to 24 h and gave equivalent yields. A solution of 50 g (0.3 mol) of ethyl 1-cyanocyclopentanecarboxylate and 14.7 g (0.3 mol) of NaCN in 200 mL of Me_2SO was heated at 170 °C for 2 h under reflux. The black reaction mixture was allowed to cool, diluted with three volumes of water, and extracted thoroughly with ether. The ether layers were combined, dried, and evaporated. The residue was distilled, and the fraction boiling at the literature[28] boiling point (168 °C) was collected to give 21.4 g (75%) of cyclopentanecarbonitrile as a colorless liquid which was pure by GC.

2-Methyl-2-phenylcyclohexylidenemalononitrile was prepared from 2-methyl-2-phenylcyclohexanone[14] and malononitrile by a previously published procedure.[15] The yield of 36% was duplicated, bp 155–157 °C (0.5 mm) [lit.[15] bp 150–151 °C (0.1 mm)].

1-Methylcyclopentanecarbonitrile. A solution of lithium diisopropylamide was prepared by stirring 5.6 g (0.8 mol) of lithium wire with 62.8 g (0.4 mol) of bromobenzene in 250 mL of ether with cooling for 30–45 min and then adding 40.4 g (0.4 mol) of diisopropylamine cautiously. This solution was poured slowly into a mechanically stirred solution of 22 g (0.4 mol) of propionitrile and 86.4 g (0.4 mol) of 1,4-dibromobutane in 200 mL of ether in a dry ice bath. The mixture was stirred for 1 h at dry ice temperature, for 1 h at room temperature, then cooled to dry ice temperature again, and a solution of base prepared similarly to that above was added. The mixture was stirred for 3 h in the dry ice bath and then allowed to stand overnight. The solution was quenched carefully with water, washed with water and brine, dried, and evaporated. The residue was distilled, and the fraction boiling at 59–77 °C (20 mm) was collected, giving 27.4 g (63%) of 1-methylcyclopentanecarbonitrile, 94% pure by GC; IR (film) 3.40, 4.50, little absorption beyond 7 μm; NMR (CCl_4) δ 1.40 (s, 3 H, Me), 1.5–2.3 (m, 8 H, cyclopentyl).

Anal. Calcd for $C_7H_{11}N$: 109. Found: *m/e* 109. This sample was used directly in the next step.

α-Cyano-β-(1-methylcyclopentyl)cinnamonitrile. A solution of phenyllithium was prepared by stirring 4.2 g (0.6 mol) of lithium wire with 47.1 g (0.3 mol) of bromobenzene in 200 mL of ether with cooling for 30 min. The solution was cooled to dry ice temperature, and crude 1-methylcyclopentanecarbonitrile (30 g, 0.3 mol) was added and stirred for 20 min, followed by 41 g (0.6 mol) of malononitrile added all at once quickly. The mixture was allowed to warm to room temperature and then was quenched with water, washed thoroughly with water and brine, dried, and evaporated.[8b] Recrystallization from methanol gave 16.5 g (26%) of white crystals, mp 57–58 °C; IR 3.30, 3.40, 4.53, 6.05, 6.35, 6.72, 13.40, 14.25 μm; NMR ($CDCl_3$) δ 1.2–2.3 (m, 11 H, aliphatic with methyl signal protruding at δ 1.64), 7.10–7.50 (m, 5 H, aryl).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85; MW 236. Found: C, 81.55; H, 6.62; N, 11.61; *m/e* 236.

2-Cyano-3-(1-methylcyclopentyl)indenone (3). α-Cyano-β-(1-methylcyclopentyl)cinnamonitrile (16 g, 68 mmol) was stirred in 120 mL of concentrated sulfuric acid at 50 °C for 15 min,[8] poured into 500 mL of ice, collected, washed with water, and recrystallized from methanol to afford 6.13 g (38%) of yellow cyrstals, mp 137–138 °C; IR (KBr) 3.45, 4.54, 5.85, 6.27, 6.42, 6.90 μm; NMR ($CDCl_3$) δ 1.57 (s, 3 H, Me), 1.7–2.6 (m, 8 H, cyclopentyl), 7.62 (s, 4 H, aryl).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90; MW 237. Found: C, 81.04; H, 6.09; N, 6.15; *m/e* 237.

4a-Methyl-9-oxo-10-cyano-1,2,3,4,4a,9-hexahydrophenanthrene (4). A solution of **3** (7.0 g, 30 mmol) in 70 mL of concentrated sulfuric acid was stirred at room temperature for 1 h,[7] poured over ice, extracted with ether, filtered, and the residue triturated with ether, which was combined with the ether extracts. The combined ether extracts were washed with water, 5% $NaHCO_3$, and brine, dried, and evpaorated. Recrystallization of the residue (4.50 g, 65%) from cyclohexane gave white crystals, mp 90–91 °C; IR (KBr) 3.42, 4.51, 6.07, 6.24, 6.38 sh, 6.90 μm; NMR ($CDCl_3$) δ 1.0–3.0 (m, 11 H, aliphatic with methyl signal protruding at δ 1.53), 7.2–7.8 (m, 3 H, aryl), 8.31 (d, J = 7 Hz, 1 H, aryl *peri*- to C=O). It was found that traces of acid present during recrystallization caused decomposition, and it was necessary to wash the crude product several times before recrystallization was carried out.

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90; MW 237. Found: C, 80.88; H, 6.57; N, 6.19; *m/e* 237.

4a-Methyl-9-oxo-10,10a-dicyano-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (7). A mixture of 80 mL of *tert*-butyl alcohol, 20 mL of water, 4.6 g (20 mmol) of **4** and excess (1.5 g) sodium cyanide was refluxed overnight.[23] Most of the solvent was then evaporated, and the residue was cooled, acidified with acetic acid, and extracted quickly with ether. The ether layers were washed with water and brine, dried, and evaporated. Recrystallization of the residue with cyclohexane and a little chloroform resulted in a gummy oil that deposited on cooling, which on addition of a few drops of chloroform with stirring gave 4.61 g (90%) of a fine white powder, mp 162.0–163.5 °C; IR (KBr) 3.1 brd, 3.45, 4.55 s, 5.91 w, 6.15 s, 6.40, 6.77 μm; NMR ($CDCl_3$) δ 1.5–2.5 (m, 11 H, alkyl), 4.67 (s, 0.5 H, H adjacent to C=O), 5.35 (low and rounded, 0.5 H, enolic), 7.5–8.5 (m, 4 H, aryl).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; MW 264. Found: C, 76.92; H, 6.03; N, 10.37; *m/e* 264.

Retro-Michael Reaction of 7 to 4. A solution of 1.04 g (4 mmol) of **7** and excess (2.00 g) hydrazine hydrate in 60 mL of ethanol was heated to reflux. Then a small drop of acetic acid was added, and the reflux was continued overnight. The ether extract of the cooled solution was washed with brine, dried with K_2CO_3, and evaporated. The residue was purified by column chromatography (silica gel, chloroform) to give 0.50 g (49%) of **4** as the first material off with spectra and melting point similar to those given above.

4a-Methyl-9-methoxy-10,10a-dicyano-1,2,3,4,4a,10a-hexahydrophenanthrene (8). To a solution of 1.04 g (4 mmol) of **7** in 50 mL of Me_2SO was added excess (1.6 g) methyl iodide and 0.008 mL (0.96 g) of potassium *tert*-butoxide. After stirring overnight at room temperature, the mixture was diluted with three volumes of water and extracted with ether. The ether extracts were washed with water and brine, dried, and evaporated. Recrystallization of the residue from methanol gave 0.59 g (54%) of white crystals, mp 118.5–119.0 °C; IR (KBr) 3.44, 4.56, 6.20, 6.41 μm; NMR ($CDCl_3$) δ 1.2–2.5 (m, 11 H, alkyl), 4.31 (s, 3 H, MeO), 7.3–8.1 (m, 4 H, aryl).

Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06; MW 278. Found: C, 77.47; H, 6.62; N, 10.35; *m/e* 278.

α-Cyano-β-(1-phenylcyclopentyl)crotononitrile (9). In 20 mL of THF cooled to −78 °C was placed 0.02 mol (11.8 mL of 1.7 M solution) of methyllithium followed by 3.42 g (20 mmol) of 1-phenylcyclopentanecarbonitrile. After stirring for 20 min at room temperature, the mixture was cooled again and excess (2.7 g) malononitrile was added all at once quickly. After the usual workup[8b] the residue was distilled to give 2.15 g (46%) of a colorless, viscous oil, bp 134–136 °C (0.07 mm); IR 3.40, 4.51 s, 6.32, 6.71, 13.50, 14.30 μm; NMR ($CDCl_3$) δ 1.2–2.9 (m, 11 H, alkyl with methyl singlet protruding at δ 2.26), 7.40 (s, 5 H, aryl).

Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85; MW 236. Found: C, 81.11; H, 6.94; N, 11.92; *m/e* 236.

Spiro[cyclopentane-1,1′(2′*H*,3′*H*,4′*H*)-naphthalen]-4′-one (11). This material was prepared from 2-phenylcyclopentanone as previously reported[17] without isolation of the intermediate **10** or its reduction product. The overall yield was 40%, obtained as a colorless, neutral liquid, bp 149–150 °C (3 mm) [lit.[17] bp 131–132 °C (2 mm)]; IR 3.41, 5.92, 6.25, 6.80 μm; NMR (CCl_4) δ 1.82 (m, 10 H, alkyl), 2.56 (distorted t, 2 H, J = 6 Hz, α-CH_2), 7.30 (m, 3 H, aryl), 7.93 (m, 1 H, *peri*-).

3′-Bromospiro[cyclopentane-1,1′(2′*H*,3′*H*,4′*H*)-naphthalen]-4′-one (12). Treatment of **11** in carbon tetrachloride with bromine vapor in a nitrogen stream[17] gave this compund in nearly quantitative yield, obtained as white crystals from methanol (*irritant!*), mp 54.0–54.5 °C (lit.[17] mp 54–55 °C); NMR ($CDCl_3$) δ 1.90 (m, 8 H, cyclopentyl), 2.60 (d, 2 H, J = 9 Hz, CH_2), 5.09 (t, 1 H, J = 9 Hz, α-H),

7.2–7.7 (m, 3 H, aryl), 8.12 (m, 1 H, *peri*-).

Spiro[cyclopentane-1,1′(4′*H*)-naphthalen]-4′-one (13). To a solution of 5.60 g (20 mmol) of **12** in 100 mL of DMF was added 16 g of lithium bromide and 10 g of lithium carbonate.[18] The resulting suspension was stirred at 100 °C overnight under nitrogen, cooled, poured into water, and extracted with ether. The ether was washed with brine, dried, and evaporated. Distillation of the residue gave 3.18 g (80%) of **13** as a colorless oil, which crystallized when scratched after standing in the refrigerator overnight, bp 140 °C sharp (1.3 mm) [lit.[17] bp 147 °C (2 mm)]; mp 32–34 °C; IR 3.40, 6.00, 6.13, 6.24, 6.76 μm; NMR ($CDCl_3$) δ 2.00 (s, 8 H, cyclopentyl), 6.19 (d, 1 H, J = 10 Hz, vinyl), 6.90 (d, 1 H, J = 10 Hz, vinyl), 7.41 (m, 3 H, aryl), 8.10 (broadened d, 1 H, J = 7 Hz, *peri*-).

3-Methylcyclohex-2-enone (15). Using technical formaldehyde, a yield of 43% of **15** was obtained by the published procedure[20] as a colorless liquid, bp 82–84 °C (12.3 mm) [lit.[20] bp 195–202 °C].

6-Methyl-2-oxo-7-oxabicyclo[4.1.0]heptane (16). The epoxidation method described by Wasson and House[25] (alkaline hydrogen peroxide in methanol) was applied to **15.** The reaction time was shortened from 3 to 1.5 h, to give 58% of **16** as a colorless liquid, bp 80–82 °C (12.4 mm) [lit.[21] bp 201–202 °C].

3-Methyl-2,3-dicyanocyclohexanone (21). To 5.0 g (0.1 mol) of sodium cyanide in 100 mL of methanol at room temperature was added 6.3 g (50 mmol) of **16.** The mixture was refluxed for 2 h, after which most of the solvent was evaporated (the salt **20** precipitated), and the residue was diluted with water. The aqueous solution was washed with ether to remove any neutral impurities and then acidified. The ether extract of the acidified solution was washed with water and brine, dried, and evaporated. Recrystallization of the residue from benzene gave 4.6 g (57%) of **21** as an almost white powder, mp 106–107 °C; IR (KBr) 2.92, 3.40, 4.47, 5.82, 6.1 sh μm; NMR ($CDCl_3$ with some acetone-d_6) δ 1.5–2.9 (m, 9 H, alkyl with methyl signal protruding at δ 1.66), 4.00 (brd s, 0.2–0.3 H, α-H), 4.21 (brd s, 0.1 H, α-H), 7.4–8.0 (low, rounded, 0.7 H, OH of enol).

Anal. Calcd for $C_9H_{10}N_2O$: C, 66.64; H, 6.21; N, 17.28; MW 162. Found: C, 66.49; H, 6.12; N, 17.38; *m/e* 162.

2′-Methylspiro[cyclopentane-1,1′(2′*H*,3′*H*,4′*H*)-naphthalen]-4′-one (22). To a suspension of 3.81 g (20 mmol) of cuprous iodide in 100 mL of dry ether at 0 °C under nitrogen was added methyllithium (1.7 M solution in ether) until a clear solution was obtained. A few crystals of cuprous iodide were then added to ensure[26] the absence of excess methyllithium (a yellow precipitate of methylcopper was observable), and the mixture was then stirred an additional 15 min at 0 °C. The enone **13** (0.01 m, 198 g) was then added in a little ether (a transient reddish color was observed on contact), and the resulting yellow mixture was stirred at 0 °C for 1 h. The mixture was quenched by pouring it into 10% aqueous ammonia, and the separated ether layer was washed with 10% aqueous ammonia and brine, dried, and evaporated. Distillation of the residue gave 2.0 g (93%) of **22** as a colorless oil, bp 137–139 °C (1.5 mm); IR 3.40, 5.90, 6.27, 6.80 μm; NMR (CCl_4) δ 0.7–3.2 (m, 12 H, alkyl with methyl doublet, J = 7 Hz, protruding at δ 0.90 and doublets, J = 5 Hz, protruding at δ 2.47 and 2.70 from the CH_2 adjacent to the carbonyl), 7.1–7.6 (m, 3 H, aryl), 7.85–8.15 (m, 1 H, *peri*-).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47; MW 214. Found: C, 83.81; H, 8.31; *m/e* 214.

2,4-dinitrophenylhydrazone derivative: orange crystals from ethanol and ethyl acetate, mp 166.0–166.5 °C.

2′-Methyl-3′-bromospiro[cyclopentane-1,1′(2′*H*,3′*H*,4′*H*)-naphthalen]-4′-one (23). The same method used to obtain **12** was applied to **22.** From 1.07 g (5 mmol) of **22** was obtained 1.54 g of crude product as an oil. Recrystallization of a sample from methanol gave nearly white crystals of **23,** mp 53–54 °C; IR (KBr) 3.40, 5.87, 6.24, 6.80 μm; NMR ($CDCl_3$) δ 1.08 (d, 3 h, J = 7 Hz, Me), 1.6–2.8 (m, 9 H, alkyl), 5.40 (d, 1 H, J = 4 Hz, α-H), 7.1–7.7 (m, 3 H, aryl), 7.9–8.2 (m, 1 H, *peri*-).

Anal. Calcd for $C_{15}H_{17}BrO$: C, 61.44; H, 5.85; Br, 27.26; MW 293. Found: C, 61.43; H, 5.90; Br, 26.98; *m/e* 293.

2′-Methylspiro[cyclopentane-1,1′(4′*H*)-naphthalen]-4′-one (24). The same method used to obtain the enone **13** was applied to **23.** From 1.1 g of crude **23** was obtained 0.63 g (80%) of **24.** A portion was recyrstallized from hexane with difficulty to give light yellow crystals, mp 65.6–66.5 °C; IR (KBr) 3.40, 6.07, 6.26, 6.87 μm; NMR ($CDCl_3$) δ 2.12 (s, 11 H, alkyl), 6.32 (s, 1 H, vinyl), 7.3–7.7 (m, 3 H, aryl), 8.1–8.3 (m, 1 H, *peri*-).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60; MW 212. Found: C, 84.52; H, 7.45; *m/e* 212.

2′-Methyl-2′,3′-dicyanospiro[cyclopentane-1,1′(2′*H*,3′*H*,4′*H*)-naphthalen]-4′-one (25). The enone **24** was treated with alkaline hydrogen peroxide,[25] and the crude epoxide was then treated with sodium cyanide by the same procedure used to obtain the dinitrile **21.** From 0.38 g of crude **24** was obtained, after recrystalization from cyclohexane with a little chloroform, 0.16 g (34%) of **25** as white crystals, mp 169–170 °C; IR (KBr) 3.1–3.2, 3.40, 4.54, 5.89, 6.19, 6.40, 6.80 μm; NMR (acetone-d_6) δ 0.6–2.2 (m, 11 H, alkyl with methyl signals protruding at δ 1.52, 1.55, and 1.59), 4.70 (brd s, 0.2 H, α-H), 6.8–7.7 (m, 4 H, aryl).

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60; MW 264. Found: C, 77.25; H, 6.15; N, 10.44; *m/e* 264.

1-Benzylcyclopentanecarbonitrile (26a). A solution of 1.9 g (20 mmol) of cyclopentanecarbonitrile and 2.53 g (20 mmol) of benzyl chloride in THF (50 mL) was cooled to −78 °C under nitrogen. A solution of lithium diisopropylamide, prepared by adding 2.02 g (20 mmol) of diisopropylamine to 0.02 mol of butyllithium (12.5 mL of 1.6 M solution in hexane) in 20 mL of THF, was cooled to −78 °C in a separate vessel. The solutions were quickly mixed, and the resulting mixture was kept at −78 °C for 3 h and then allowed to stand at room temperature overnight. The mixture was quenched with water, washed with brine, dried, and evaporated. Distillation of the residue gave 2.24 g (61%) of **26a** as a colorless liquid, bp 127–129 °C (2.8 mm) [lit.[31] bp 155–157 °C (12 mm)]; IR 3.30, 3.39, 4.47, 6.24, 6.70, 13.10, 14.26 μm; NMR (CCl_4) δ 1.80 (brd s, 8 H, cyclopentyl), 2.81 (s, 2 H, benzylic), 7.25 (s, 5 H, aryl).

1-Methoxymethylcyclopentanecarbonitrile (26b). By the above method using 1.61 g (20 mmol) of methyl chloromethyl ether as the halide was obtained 0.87 g (31%) of **26b** as a colorless liquid, bp 106–108 °C (20 mm); IR 3.40, 4.49, 9.0 μm; NMR (CCl_4) δ 1.82 (brd s, 8 H, cyclopentyl), 3.35 and 3.40 (overlapping s, 5 H, Me and CH_2).

Anal. Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06; MW 139. Found: C, 68.83; H, 8.92; N, 9.80; *m/e* 139.

1-Methoxyethylcyclopentanecarbonitrile (26c). By the above method using 1.90 g (20 mmol) methyl 2-chloroethyl ether (prepared from the corresponding alcohol with phosphorus trichloride[34]) was obtained 1.00 g (33%) of **26c** as a colorless liquid of 98% purity by GC, bp 118–120 °C (20 mm); IR 3.40, 4.50, 8.9 μm; NMR δ 1.3–2.4 (m, 10 H, cyclopentyl and branch CH_2), 3.33 (s, 3 H, Me), 3.59 (t, 2 H, J = 7 Hz, CH_2O).

Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14; MW 153. Found: C, 70.39; H, 9.85; N, 9.20; *m/e* 153.

α-Cyano-β-(1-benzylcyclopentyl)cinnamonitrile (27a). Phenyllithium was generated by stirring 0.02 mol (12.50 mL of a 1.6 M solution) of butyllithium in hexane with 3.14 g (20 mmol) of bromobenzene in 20 mL of THF at −78 °C for 15 min. Then 3.70 g (20 mmol) of **26a** was added, and the mixture was stirred for 20 min without any outside cooling, cooled again to −78 °C, and quenched with 2.7 g (40 mmol) of malononitrile.[8b] The solution was allowed to warm to room temperature and then quenched with water, washed with brine, dried, and evaporated. Recrystallization of the residue from methanol gave 3.81 g (61%) of **27a** as white needles, mp 115–116 °C; IR (KBr) 3.41, 4.50, 6.45, 6.75, 13.19, 13.90, 14.35 μm; NMR ($CDCl_3$) δ 1.5–2.3 (m, 8 H, cyclopentyl), 3.27 (s, 2 H, benzyl), 6.44 (m, 2 H, aryl ortho on one of the rings), 7.34 (m, 8 H, aryl).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97; MW 312. Found: C, 84.38; H, 6.27; N, 8.97; *m/e* 312.

α-Cyano-β-(1-methoxymethylcyclopentyl)cinnamonitrile (27b). By the above method using 2.78 g (20 mmol) of **26b, 27b** was obtained (3.85 g, 72%) as white crystals from methanol, mp 99–100 °C; IR (KBr) 3.50, 4.54, 6.45, 6.80, 13.15, 13.99, 14.35 μm; NMR ($CDCl_3$) δ 1.5–2.2 (m, 8 H, cyclopentyl), 3.45 (s, 3 H, MeO), 3.67 (s, 2 H, CH_2O), 7.2–7.7 (m, 5 H, aryl).

Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.51; MW 266. Found: C, 76.32; H, 6.54; N, 10.28; *m/e* 266.

α-Cyano-β-(1-benzylcyclopentyl)-*p*-methoxycinnamonitrile (27d). By the method used for the preparation of **27a** using 3.74 g (20 mmol) of *p*-bromoanisole instead of bromobenzene was obtined 5.06 g (74%) of **27d** as white crystals from ethanol, mp 125.0–125.5 °C; IR (KBr) 3.40, 4.50, 6.25, 6.70 μm; NMR ($CDCl_3$) δ 1.7–2.5 (m, 8 H, cyclopentyl), 3.35 (s, 2 H, benzyl), 3.85 (s, 3 H, MeO), 6.43 (d, 2 H, J = 8 Hz, aryl ortho to MeO), 6.88 (d, 2 H, J = 8 Hz, aryl ortho to C=C), 7.5–8.0 (m, 5 H, aryl).

Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.47; N, 8.18; MW 342. Found: C, 80.83; H, 6.72; N, 8.00; *m/e* 342.

α-Cyano-β-(1-phenylcyclopentyl)cinnamonitrile (27e). By the method used for the preparation of **27a** using 1-phenylcyclopentanecarbonitrile (**26d**) instead of **26a** was obtained 2.30 g (39%) of **27e** as white crystals from methanol (after previously heating the crude product under vacuum), mp 87.5–88.5 °C; IR 3.40, 4.50, 6.40, 6.75 μm; NMR ($CDCl_3$) δ 1.4–2.7 (m, 8 H, cyclopentyl), 6.8–7.6 (m, 10 H, aryl).

Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39; MW 298. Found: C, 84.76; H, 5.73; N, 9.56; *m/e* 298.

β-(1-Hydroxymethylcyclopentyl)-α-cyano-*trans*-cinnamic Acid Lactone (29). A solution of 1.00 g (3.8 mmol) of **27b** in 7 mL of concentrated sulfuric acid was maintained at 50 °C for 15 min and then poured over ice. The combined organic layers from benzene and THF extractions were washed with 5% $NaHCO_3$, dried, and evaporated. Recrystallization of the residue from methanol gave 0.11 g (12%) of **29** as white crystals, mp 166.0–167.5 °C; IR (KBr) 3.41, 4.51, 5.81, 6.30, 6.85, 13.29, 14.15 μm; NMR ($CDCl_3$) δ 1.78 (s, 8 H, cyclopentyl), 4.31 (s, 2 H, CH_2), 7.2–7.7 (m, 5 H, aryl).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53; MW 253. Found: C, 75.73; H, 5.79; N, 5.80; *m/e* 253.

Registry No.—**3,** 64871-55-2; **4,** 64871-56-3; **7,** 64871-57-4; **8,** 64871-58-5; **9,** 64871-59-6; **11,** 4889-95-6; **12,** 64871-60-9; **13,** 64871-61-0; **15,** 1193-18-6; **16,** 21889-89-4; **21,** 64871-62-1; **22,** 64871-63-2; **22**-DNP, 64871-64-3; **23,** 64871-65-4; **24,** 64871-72-3; **25,** 64871-73-4; **26a,** 64871-66-5; **26b,** 64871-74-5; **26c,** 64871-75-6; **26d,** 77-57-6; **27a,** 64871-76-7; **27b,** 64871-77-8; **27d,** 64871-78-9; **27e,** 64871-67-6; **29,** 64871-68-7; phenylacetonitrile, 140-29-4; 1,4-dichlorobutane, 110-56-5; cyclopentanecarbonitrile, 4254-02-8; ethyl 1-cyanocyclopentanecarboxylate, 28247-14-5; 1,4-dibromobutane, 110-52-1; 2-methyl-2-phenylcyclohexylidenemalononitrile, 64871-69-8; 1-methylcyclopentanecarbonitrile, 64871-70-1; propionitrile, 107-12-0; α-cyano-β-(1-methylcyclopentyl)cinnamonitrile, 64871-71-2; phenyllithium, 591-51-5; malononitrile, 109-77-3; sodium cyanide, 143-33-9; methyl iodide, 74-88-4; benzyl chloride, 100-44-7; methyl chloromethyl ether, 107-30-2; methyl 2-chloroethyl ether, 627-42-9; bromobenzene, 108-86-1; *p*-bromoanisole, 104-92-7.

References and Notes

(1) (a) Cyclization of Ylidenemalononitriles, 9. Supported in part by Grant GM-10366 from the National Institutes of Health. Part 8: E. Campaigne and Dale E. Mais, *J. Heterocycl. Chem.*, **12,** 267 (1975). (b) Submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy, Indiana University, July 1977.
(2) M. Menard et al., *Can. J. Chem.*, **54,** 429 (1976).
(3) I. Monkovic and H. Wong, *Can. J. Chem.*, **54,** 883 (1976).
(4) I. Monkovic et al., *Can. J. Chem.*, **53,** 2515 (1975).
(5) I. Monkovic et al., *Can. J. Chem.*, **53,** 3094 (1975).
(6) B. Belleau et al., *Can. J. Chem.*, **53,** 237 (1975).
(7) E. Campaigne and D. Maulding, *J. Org. Chem.*, **28,** 1391 (1963).
(8) (a) E. Campaigne and S. Schneller, *Synthesis,* 705 (1976); (b) E. Campaigne, D. Mais, and E. M. Yokley, *Synth. Commun.*, **4,** 379 (1974).
(9) T. Zalesskaya and O. Netsetskaya, *J. Org. Chem. USSR (Engl. Transl.)*, **5,** 1563 (1969).
(10) M. Larcheveque, P. Mulot, and T. Cuvigny, *J. Organomet. Chem.*, **57,** C33 (1973).
(11) C. Tilford, M. Van Campen, Jr., and R. Shelton, *J. Am. Chem. Soc.*, **69,** 2902 (1947).
(12) N. Sperber, D. Papa, and E. Schwenk, *J. Am. Chem. Soc.*, **70,** 3091 (1948).
(13) E. Campaigne et al., *J. Heterocycl. Chem.*, **8,** 65 (1971).
(14) S. Kulp et al., *J. Org. Chem.*, **40,** 453 (1975).
(15) T. Sasaki, K. Kanematsu, and K. Minamoto, *Yakugaku Zasshi,* **84,** 381 (1964); *Chem. Abstr.*, **61,** 4285b (1964).
(16) M. Makosza and B. Serafin, *Rocz. Chem.*, **40,** 1647 (1966); *Chem. Abstr.*, **66,** 94792x (1967).
(17) R. Arnold, J. Buckley, Jr., and R. Dodson, *J. Am. Chem. Soc.*, **72,** 3153 (1950).
(18) T. Payne and P. Jefferies, *Tetrahedron,* **29,** 2575 (1973).
(19) A. Platé et al., *J. Gen. Chem. USSR (Engl. Transl.)*, **30,** 1273 (1960).
(20) S. Natelson and S. Gottfried, *J. Am. Chem. Soc.*, **61,** 1001 (1939).
(21) W. Treibs, *Ber. Dtsch. Chem. Ges. B,* **66,** 1483 (1933).
(22) J. Huffman and T. Bethea, *J. Org. Chem.*, **30,** 2956 (1965).
(23) E. Campaigne and W. Roelofs, *J. Org. Chem.*, **30,** 2610 (1965).
(24) (a) V. Grignard and K. Ono, *Bull. Soc. Chim. Fr.*, **39,** 1593 (1926); (b) M. Newman and R. Closson, *J. Am. Chem. Soc.*, **66,** 1553 (1944).
(25) R. Wasson and H. House, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 552.
(26) E. Piers, W. de Waal, and R. Britton, *J. Am. Chem. Soc.*, **93,** 5113 (1971).
(27) L. Friedman and H. Shechter, *J. Org. Chem.*, **25,** 878 (1960).
(28) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, **16,** 470 (1949).
(29) P. Mueller and B. Siegfried, *Tetrahedron Lett.*, 3565 (1973).
(30) A. Krapcho and A. Lovey, *Tetrahedron Lett.*, 957 (1973).
(31) C. Tilford, M. Van Campen, Jr., and R. Shelton, *J. Am. Chem. Soc.*, **69,** 2902 (1947).
(32) E. Campaigne and D. Mais, *J. Heterocycl. Chem.*, **12,** 267 (1975).
(33) W. Bailey and J. Daly, Jr., *J. Am. Chem. Soc.*, **81,** 5397 (1959).
(34) M. Palomaa and A. Kenetti, *Ber. Dtsch. Chem. Ges. B,* **64,** 798 (1931).

Ring Expansions of Medium-Sized Ring Potassium Alkoxides. Unusually Fast [1,3]Sigmatropic Shifts

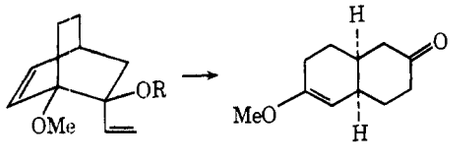
Richard W. Thies* and E. Philip Seitz

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Received July 29, 1977

A series of cyclic 1-vinyl alcohols having either a double bond or a benzo group at the 3 position were rearranged under the influence of potassium hydride to the ring-expanded ketones, e.g., 1-vinylcyclonon-3-en-1-ol to 5-cycloundecenone. In hexamethylphosphoric triamide (HMPT) or dimethoxyethane (DME)/18-crown-6 media, the [1,3]sigmatropic shifts take place at room temperature. 1-Cyclopropyl analogues undergo ring cleavage rather than rearrangement.

Evans and Golob recently reported[1] that the bicyclic oxy-Cope system (1) underwent a [3,3]sigmatropic rearrangement



1a, R = H
b, R = K

at an enormously enhanced rate when treated with potassium hydride in tetrahydrofuran (THF) or HMPT. The epimer of **1**, where the geometry precludes a concerted 3,3-shift process, was reported to not rearrange when treated with potassium hydride in refluxing THF. Although [1,3]sigmatropic shifts are possible for 1 and its epimer, none were reported. It was not clear whether 1,3 shifts should be enhanced since they generally show activation parameters that are more suggestive of a nonconcerted process than is the case for 3,3-shift processes.[2,3] We have subsequently found that 1,3 shifts in oxy-Cope[4] systems are enhanced under appropriate conditions.[4,5]

Our previous studies[2,6,7] have shown that 1-trimethylsiloxy-1-vinyl-3-cycloalkenes, **2** (R = $SiMe_3$), undergo thermal rearrangements at 240–300 °C which lead mainly to two-carbon ring expansion products, **3** and **4**, except for **2d**, where the 3,3-shift product **5** predominates.

We now report the reactions of the potassium alkoxides of these and the related systems **6** and **8** in highly dissociating media.

0022-3263/78/1943-1050$01.00/0