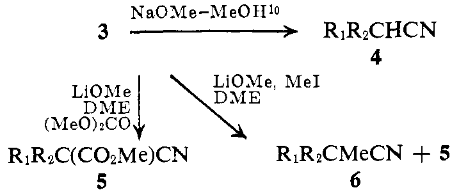
Scheme II

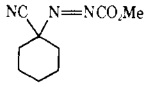
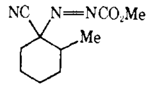
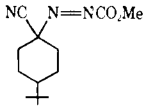


$$\begin{tikzcd} \mathbf{3} \arrow[r, "\text{NaOMe-MeOH}^{10}"] \arrow[d, "\substack{\text{LiOMe}\\ \text{DME}\\ (\text{MeO})_2\text{CO}}"'] \arrow[dr, "\substack{\text{LiOMe, MeI}\\ \text{DME}}"] & \underset{\mathbf{4}}{R_1R_2CHCN} \\ \underset{\mathbf{5}}{R_1R_2C(CO_2Me)CN} & \underset{\mathbf{6}}{R_1R_2CMeCN} + \mathbf{5} \end{tikzcd}$$

A and B can be effected either with catalytic or with larger quantities of base, whereas method C necessitates at least stoichiometric quantities of base (Scheme II).

The application of these reaction sequences on the diazenes derived from cyclohexanone, 2-methylcyclohexanone, and 4-*tert*-butylcyclohexanone is presented in Table I.

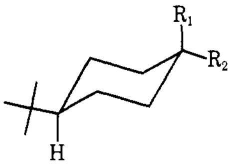
Table I. Products (Per Cent) from Diazene Decomposition[a]

Diazene (yield)[b]	Method	Nitrile	Carbomethoxy-nitrile	Methyl-nitrile
 **7** (96)	A	94	0	
	B	7	77	
	C	0	13	77
 **8** (95)	A	89[c]	0	
	C	2	25[d]	63 (**11c**/**11d** = 73/27)
 **9** (94)	A	97 (**10a**/**10b** = 58/42)	0	
	C	1	23[d]	70 (**10c**/**10d** = 76/24)

[a] All yields are absolute, employing biphenyl and/or cyclohexanone as an internal standard on an Aerograph A-90-P gas chromatograph, $^3/_8$ in. × 20 ft, 20% SE-30 on Chromosorb W (45–60 mesh) column. [b] Distilled yield based on ketone. [c] Not routinely separable by glc; nmr shows two methyl doublets (~50/50). [d] A mixture of diastereomers by glc.

The ratio of the diastereomeric pair of nitriles **10a–b** reflects the products of kinetic protonation, since subjection of the axial nitrile **10a** to the original alkaline reaction conditions showed no sign of equilibration. However, treatment of the kinetic mixture (**10a**/**10b** = 58/42) with potassium *tert*-butoxide–*tert*-butyl alcohol produced the thermodynamic mixture, cis–trans (45:55) (lit.[11] 44:56).[12]

The *in situ* methylation with diazenes **8** and **9** provided predominantly the products from equatorial methylation. The ratio 76:24 (**10c**:**10d**) is in accord with the observed product distribution (71:29) from the methylation of the anion of the 4-*tert*-butylcyclohexylnitrile generated with lithium diethylamide.[13] The identity of nitrile **11d** was confirmed by synthesis from the Diels–Alder adduct of tiglic acid and butadiene.[14]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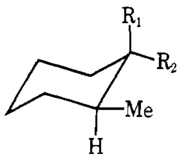
11

a, $R_1 = CN$; $R_2 = H$
b, $R_1 = H$; $R_2 = CN$
c, $R_1 = CN$; $R_2 = Me$
d, $R_1 = Me$; $R_2 = CN$

The procedure for transforming ketones into nitriles is particularly suited for preparative purposes. Thus, cyclohexanone was converted to cyclohexylnitrile in 80% yield (distilled) without purification of the intermediates.

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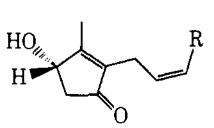
A New Synthesis of Rethrolones

Sir:

Rethrolones are the alcohol components of the pyrethrins,[1] a group of naturally occurring esters of chrysanthemic and pyrethric acid with useful insecticidal properties. Contrary to other, in many instances more potent insecticides, the pyrethrins are biodegradable and of low mammalian toxicity. These desirable properties undoubtedly are responsible for renewed interest in the chemical synthesis of pyrethrins. While efficient routes to chrysanthemic acid have been developed,[2] syntheses of rethrolones, with the exception of a recent preparation by Crombie and coworkers,[3] have been troubled by low yields. This paper describes a synthesis of rethrolones which has novel features and yields, *e.g.*, allethrolone (**1**) in 36% yield from readily available allylacetylacetone (**3**).


1, R = H
2, R = CH_3

Ketal exchange[4] between 3 equiv of 2,2-dimethoxypropane and 1 equiv of the diketone **3** in benzene solution at reflux in the presence of a trace of *p*-toluenesulfonic acid gave a mixture of products (87%) containing 90% monoketal **4**, 7% vinyl ether **5**, and 3% of the vinylogous ester **7**. Distillation (bp 52–58° (1.8 mm))

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(10) Deuterium can be cleanly incorporated at the α position by employing sodium methoxide in methanol-d_1.

(11) B. Rickborn and F. R. Jensen, *J. Org. Chem.*, **27**, 4606 (1962).

(12) A similar experiment could be conducted with **11a, b** in a qualitative fashion by observing the change in the methyl doublet patterns in the nmr spectrum of the mixture.

(13) H. O. House and T. M. Bare, *J. Org. Chem.*, **33**, 943 (1968).

(14) H. O. House and W. F. Gilmore, *J. Amer. Chem. Soc.*, **83**, 3980 (1961).

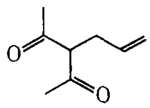
(1) L. Crombie and M. Elliott, *Fortschr. Chem. Org. Naturst.*, **19**, 121 (1961).

(2) For the latest preparations see M. Julia and A. Guy-Rouault, *Bull. Soc. Chim. Fr.*, 1411 (1967); E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967); R. W. Mills, R. D. H. Murray, and R. A. Raphael, *Chem. Commun.*, 555 (1971).

(3) L. Crombie, P. Hemesley, and G. Pattenden, *J. Chem. Soc. C*, 1016 (1969).

(4) N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960).

of crude ketal over a catalytic amount of anhydrous *p*-toluenesulfonic acid produced a mixture of the vinyl ether **5** (64%) (ir (CCl_4) 1720 cm^{-1}; nmr ($CDCl_3$) δ 3.00 (m, 1), 4.06 (s, 2), etc.) and the stereoisomeric β-methoxy-α,β-unsaturated ketones **7** (18%) (ir (CCl_4) 1665 cm^{-1}; uv (95% EtOH) 273 nm (ϵ 14,200)) separable by vapor phase chromatography. The distribution of isomers **5** and **7** observed is the result of a kinetic effect because *p*-toluenesulfonic acid catalyzed equilibration in refluxing tetrahydrofuran leads to an equilibrium mixture containing 65% of the conjugated (**7**) and 35% of the unconjugated isomer (**5**) (uv *and* vpc analysis). Condensation of the ketone **5** with dichloromethyllithium[5] gave the sensitive chloroepoxide **8** which was hydrolyzed directly (20°, 45 min) in 2:1 tetrahydrofuran–10% aqueous hydrochloric acid to the equally sensitive ketone **9** (ir (CCl_4) 1720 cm^{-1}). While the enol ether **8** was stable to 0.1 *M* aqueous methanolic barium hydroxide at room temperature, cyclization of the corresponding ketone **9** under identical conditions was complete within 1 hr giving allethrolone (**1**) (72% based on **5**) (ir (CCl_4) 3430, 1705, 1645 cm^{-1}; uv (95% EtOH) 231 nm (ϵ 13,300)).[6] Its nmr spectrum was identical with that reported.[7] The synthesis can be performed with crude vinyl ether **5** because the vinylogous ester **7** does not combine with dichloromethyllithium. The latter is transformed to the β-diketone **3** readily separable from the rethrolone **1** by base extraction, in the course of the two subsequent hydrolytic operations.



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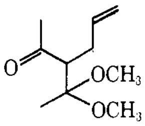

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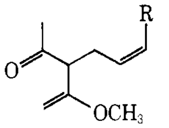
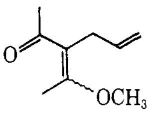


5, R = H
6, R = CH_3



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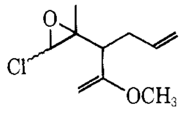

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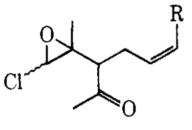
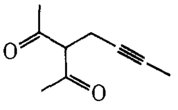


9, R = H
10, R = CH_3



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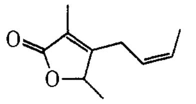

12

Alkylation of acetylacetone with 2-butynyl-*p*-toluenesulfonate[8] in aqueous methanol containing 1 equiv of Hünig's base[9] gave the cinerolone precursor **11** (44%; yield not optimized); uv (95% EtOH) 287 nm (ϵ 3200); uv (EtOH, NaOH) 303 nm (ϵ 21,000). Ketal exchange and elimination of methanol, as described for allethrolone, were followed by catalytic hydrogenation over Lindlar's catalyst. The resulting cis olefin **6** was transformed to *rac-cis*-cinerolone (**2**) in similar yield by methods detailed for allethrolone. Both ir and nmr spectra[7] were identical with those of natural (+)- and synthetic[10] (±)-*cis*-cinerolone (**2**) and identity was confirmed by thin-layer chromatography.

Parenthetically, thermolysis of the chloroepoxide **10** in refluxing xylene did not yield the corresponding α-chloroaldehyde[5] but the lactone **12** (62%) (ir (CCl_4) 1755 cm^{-1}; nmr (CCl_4) δ 1.33 (d, 3, J = 7 Hz), 1.70 (d, 3, J = 6.5 Hz), 1.77 (s, 3), 3.07 (d, 2, J = 6 Hz), 4.73 (q, 1, J = 6.5 Hz), and 5.1–5.8 (m, 2)). This seemingly new synthesis of α-butenolides is being explored further.

Acknowledgment. The authors are grateful to Hoffmann-La Roche, Inc., Nutley, N. J., for financial support and to Drs. A. Brossi and R. A. LeMahieu of that firm for samples of synthetic and natural cinerolone.

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[5] Method of G. Köbrich and W. Werner, *Tetrahedron Lett.*, 2181 (1969).

[6] For a recent synthesis of allethrolone which, however, has not been applied to the preparation of a natural rethrolone, see M. Vandewalle and E. Madeleyn, *Tetrahedron*, **26**, 3551 (1970).

[7] A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliot, and N. F. James, *ibid.*, **25**, 1738 (1969).

[8] A. Marszak-Fleury, *Ann. Chim. (Paris)*, **3**, 656 (1958). A more efficient method for the preparation of this intermediate will be described in the detailed paper.

[9] Method of K. W. Rosenmund and H. Bach, *Chem. Ber.*, **94**, 2394 (1961).

[10] Prepared according to R. A. LeMahieu, M. Carson, and R. W. Kierstead, *J. Org. Chem.*, **33**, 3660 (1968).

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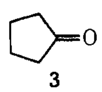
Photoelectron Spectra of Cyclopentanone and Cyclopentenones

Sir:

It is well known that the π bonds of a 1,3-unsaturated system of type **1** interact very strongly provided the two π bonds can approach coplanarity. However, when the two π bonds are "insulated" by any number of saturated

$$\underset{\textbf{1}}{C{=}C{-}C{=}X} \qquad \underset{\textbf{2}}{C{=}C{-}(C)_n{-}C{=}X}$$

atoms as is **2** then the experimental results are not always interpretable.[1] Recently, however, Heilbronner and coworkers[2] have demonstrated the utility of photoelectron spectroscopy (pes) in determining the interaction of the π bonds in systems of type **1** and **2** where X = C. Hoffmann[3] has given an extensive theoretical analysis of this phenomenon. We have been investigating the interaction of an ethylenic π bond with a carbonyl π bond, **1** and **2** where X = O, and we wish to report our results of a study of the pe spectra[4] of the series of cyclopentane derivatives **3**–**5** (Table I).



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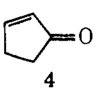

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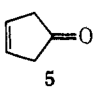

5

The first ionization potential (IP) of **3** at 9.25 eV which we assign to ionization from one of the nonbonding (n) levels has vibrational spacings of 710 and 1220 cm^{-1}. The spacing of 710 cm^{-1} in the ion is assigned to the symmetric skeletal ring breathing which is observed at 711 cm^{-1} in the Raman spectrum of the neutral molecule.[5] The vibrational spacing of 1220

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[1] L. N. Ferguson and J. C. Nnadi, *J. Chem. Educ.*, **42**, 529 (1965).

[2] E. Haselbach, E. Heilbronner, and G. Schröder, *Helv. Chim. Acta*, **54**, 153 (1971), and previous papers.

[3] R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

[4] The pe spectra were obtained using a 584-Å spectrometer with a 2-in. radius hemispherical electrostatic energy analyzer.

[5] J. R. Durig, G. L. Coulter, and D. W. Wertz, *J. Mol. Spectrosc.*, **27**, 285 (1968).