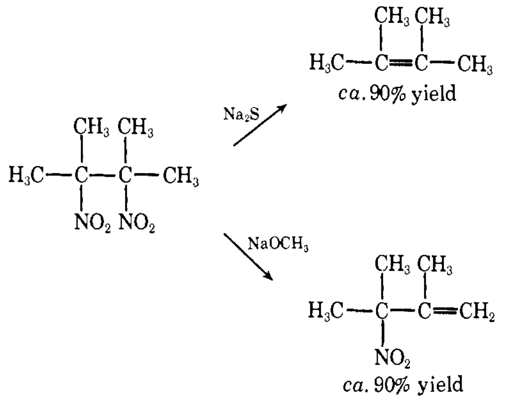
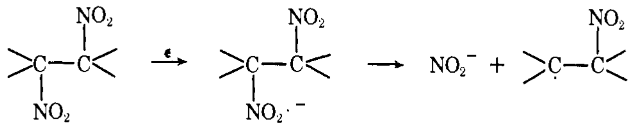
is exposed to two 20-W fluorescent lights for 12 hr. The olefin V is isolated by pouring into water, extracting with pentane, washing with water, drying over anhydrous $MgSO_4$, and carefully removing the solvent; yield 9.10 g (92%); mp 53–54°. On sublimation this gives 8.84 g of pure V (90% yield); mp 53.5–54.5°.

The elimination of two nitro groups from a vicinal dinitro compound by the agency of sodium sulfide or sodium thiophenoxide is not a simple ionic process for these reactions are unambiguously accelerated by the light of an ordinary 20-W fluorescent lamp. Also, when a strong base such as sodium methoxide is employed an alternative type of elimination reaction occurs (eq 6). These facts, and observations with other aliphatic nitro systems,[11] suggest that elimination of two nitro groups from vicinal dinitro compounds involves radical anions



(6)



Various pathways are readily envisioned for the loss of the second nitro group; there is, at present, no basis for favoring one or another of these.[12]

The synthesis of tri- and disubstituted olefins is under investigation as is the study of a number of related matters: these include the use of other reducing agents and the stereochemistry and mechanism of these processes.

Acknowledgment. We thank Eli Lilly and Company and the National Science Foundation for generous support and Mr. Leung Cheng for the preparation of a number of nitroparaffins.

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[11] N. Kornblum and S. D. Boyd, *J. Amer. Chem. Soc.*, **92**, 5784 (1970).

[12] Note Added in Proof. It has now been found that 5 mol % of di-*tert*-butyl nitroxide, 4 mol % of 1,3,5-tristrichloromethylbenzene, 1 atom % of sulfur, or 5 mol % of *m*-dinitrobenzene inhibits olefin formation by sodium thiophenoxide. Reactions employing sodium sulfide are also inhibited by di-*tert*-butyl nitroxide and by 1,3,5-tristrichloromethylbenzene. Clearly, olefin formation is a chain process.

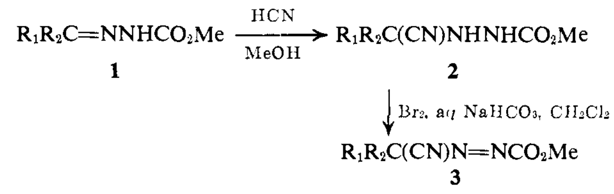
The Base-Induced Decomposition of Methyl Dialkylcyanodiazenecarboxylates. The Transformation of Ketones into Nitriles, α-Carbomethoxynitriles, and α-Methylnitriles

Sir:

The difficulties associated with effecting S_N2 displacements on secondary halides with inorganic cyanide,[1] coupled with the necessity of achieving such a transformation in our laboratory, prompted us to explore a means which would efficiently accomplish this one carbon homologation starting from a ketone. Moreover, it was deemed useful to design a scheme which would involve the intermediacy of nitrile anions, thus permitting direct alkylation. Such a technique would be of particular utility in constructing the *gem*-methylcarboxylic acid functionality present in diterpene acids[2] and steroid intermediates.[3]

Ketones are readily transformed into their carbomethoxyhydrazones (**1**),[4] which, as outlined in Scheme I, are converted in near quantitative yield to their methyl dialkylcyanodiazenecarboxylates (**3**), by successive treatment with hydrogen cyanide[5] and bromine.[5b]

Scheme I



When a 1:1 ether–methanol solution (10 ml) of the yellow diazenes **3** (20 mmol) was added dropwise (15 min, 5–10°) to a solution of sodium methoxide[6] (10 mmol) in methanol (5 ml) (method A), vigorous gas evolution (N_2) ensued with concomitant discharge of the yellow color, providing the nitriles[7] in high yields. Alternatively, when a 1,2-dimethoxyethane (DME) solution (15 ml) of the diazenes (10 mmol) was added in a dropwise fashion (25 min, 0–5°) to anhydrous lithium methoxide[8] (45 mmol) in DME (20 ml) containing dimethyl carbonate (120 mmol) (method B), the cyano esters **5** were isolated in addition to trace quantities of protonated nitriles **4**.[9] However, when methyl iodide (120 mmol) and diazene (10 mmol) in DME (20 ml) were added dropwise (1 hr, 5–10°) to lithium methoxide (45 mmol) in DME (20 ml) (method C), methylation favorably competed with carboxylation. Methods

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[1] M. F. Rogers and J. D. Roberts, *J. Amer. Chem. Soc.*, **68**, 843 (1946); R. A. Smiley and C. Arnold, *J. Org. Chem.*, **25**, 257 (1960); and L. Friedman and H. Shechter, *ibid.*, **25**, 877 (1960).

[2] M. Sharma, U. R. Ghattak, and P. C. Dutta, *Tetrahedron*, **19**, 985 (1963); *cf.* E. Wenkert, B. L. Mylari, and L. L. Davis, *J. Amer. Chem. Soc.*, **90**, 3870 (1968), and S. W. Pelletier and D. L. Herald, *Chem. Commun.*, 10 (1971).

[3] G. Stork and I. J. Borowitz, *J. Amer. Chem. Soc.*, **82**, 4307 (1960).

[4] M. C. Chaco and N. Rabjohn, *J. Org. Chem.*, **27**, 2765 (1962).

[5] *Cf.* (a) E. Mueller, H. Eck, and H. Scheurlein, French Patent 1,433,719 (1966); *Chem. Abstr.*, **65**, 16879b (1966), and (b) M. C. Ford and R. A. Rust, *J. Chem. Soc.*, 1297 (1958).

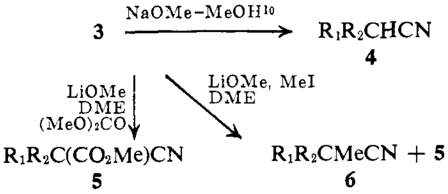
[6] For the decomposition of alkyldiazenes, see T. Tsuji and E. M. Kosower, *J. Amer. Chem. Soc.*, **93**, 1992 (1971).

[7] *Cf.* S. Goldschmidt and B. Acksteiner (*Justus Liebigs Ann. Chem.*, **618**, 173 (1958)), for the acid-catalyzed decomposition of diazenes affording nitriles.

[8] Anhydrous lithium methoxide was prepared from anhydrous methanol and butyllithium (hexane) or methyllithium (ether). Thus, the DME contained either hexane or ether as a cosolvent.

[9] The diazene can also be decomposed with anhydrous lithium iodide in DME, but at a slower rate than with lithium methoxide.

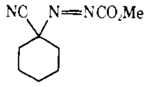
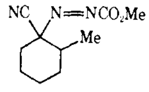
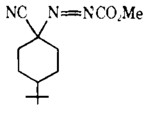
Scheme II



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.

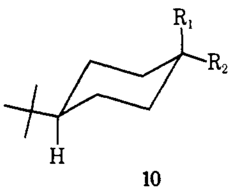
Table I. Products (Per Cent) from Diazene Decomposition[a]

Diazene (yield)[b]	Method	Nitrile	Carbo-methoxy-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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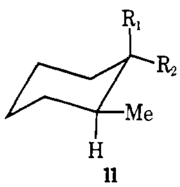

11

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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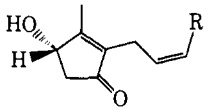
A New Synthesis of Rethrolones

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).