the polarizability without changing the dipole moment appreciably.

The only available data on the effect of alkyl groups in unsaturated systems suggest that alkyl groups bonded to unsaturated (sp or sp^2) carbon are electron releasing relative to hydrogen. These include, for example, dipole moments in toluene and methylacetylene[4] and measurements in solution in which para methyl appears to destabilize benzyl,[5] phenoxide, and benzoate anions.[6] Having previously established that gas-phase stability orders are often reversed from those in solution,[2,3] we thought it would be of value to explore the effect on acidity of alkyl groups bonded to trigonal and digonal carbon. In this communication we describe some results on the relative acidities of toluene and *p*-xylene and acetylene and substituted acetylenes, as determined by ion cyclotron resonance (icr) spectroscopy.

Experiments were carried out as described previously,[2,3] and acidity orders are inferred from the observation of the preferred direction of a reaction. We find the acidity orders ethanol > toluene > methanol > *p*-xylene > water, and acetylene > *n*-butylacetylene > methylacetylene > water.[7] Thus, in systems involving bonding to unsaturated carbon, alkyl groups relative to hydrogen appear to destabilize anions in the gas phase. Nevertheless, in accord with our observations in other systems, larger alkyl groups are stabilizing relative to smaller ones. These experimental observations are thus partially accommodated by the usual inductive picture of alkyl substituent effects, the unsaturated carbon being more electronegative, withdrawing electrons from the polarizable alkyl group, and so giving rise to a group dipole.[9,10] This dipole, then, oriented toward the localized negative charge in the anion, destabilizes the system. However, the group dipole is relatively insensitive to the size of the alkyl group,[4] so this dipolar term remains constant as the alkyl size increases. Meanwhile the larger alkyl group is more polarizable, and thus more stabilizing than a small one. Consequently, more highly substituted acetylenes are more acidic.

CNDO/2 Calculations. Because most calculations of molecule and ion stabilities refer to the isolated species, it is difficult, if not impossible, to compare the results of calculations with chemical behavior in solution. However, our gas-phase acidity orders are ideally suited for testing theory, since the species involved are precisely those whose properties are calculated. Our previous experimental results have given rise to a substantial number of calculations, both *ab initio*[11] and semiempirical,[12] all of which have confirmed our results. It has been pointed out by Jesaitis and Streitwieser[13] that some of this agreement may be fortuitous, inasmuch as certain calculations disagree with experiments, albeit in solution. We have utilized the CNDO/2 method[14] to calculate the relative acidities of acetylene and alkylacetylenes and find a predicted order of ethylacetylene > methylacetylene, but methylacetylene > acetylene in disagreement with experiment. Our experimental finding that toluene > *p*-xylene is also at variance with the CNDO/2 calculations of Streitwieser, *et al.*[15] Furthermore, the interrelationship between types of compounds is predicted badly. We calculate, for example, water > acetylene, also in disagreement with experiment.

Thus, we concur that the CNDO/2 method should only be used circumspectly, if at all, for predicting anion stabilities.[15] The reasons for the failure of this and possibly all Hartree–Fock SCF methods[11b] for calculating anion stabilities doubtless lie in the electron correlation problem, which is expected to be especially severe for negatively charged systems. Consequently, we believe that previous agreement between calculated and experimental acidity orders should probably be viewed as fortuitous until a more rigorous basis for the success (or failure) of the calculations is established.

Acknowledgment. We thank Professor J. D. Baldeschwieler for his support, J. V. Garcia for technical assistance, and Professor L. J. Altman for advice and discussions regarding the calculations. This work was supported by the National Science Foundation (GP-27532, GP-23406), the National Aeronautics and Space Administration (NGL-05-020-250), the National Institutes of Health (GM-14752), and the Center for Materials Research Stanford University.

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(4) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

(5) A. Streitwieser, Jr., and H. F. Koch, *J. Amer. Chem. Soc.*, **86**, 404 (1964).

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 142.

(7) Equilibrium acidities in solution have been determined for only a small number of acetylenes.[8] In solution acetylenes appear to be substantially less acidic than water.

(8) For recent work and references, see A. Streitwieser, Jr., and D. M. E. Reuben, *J. Amer. Chem. Soc.*, **93**, 1794 (1971).

(9) See, for example, M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(10) However, for a different view of the origin in the dipole moment of methylacetylene see (a) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967); (b) M. D. Newton and W. N. Lipscomb, *ibid.*, **89**, 4261 (1967).

(11) (a) W. J. Hehre and J. A. Pople, *Tetrahedron Lett.*, 2959 (1970); (b) P. H. Owens, R. A. Wolf, and A. Streitwieser, Jr., *ibid.*, 3385 (1970).

(12) (a) N. C. Baird, *Can. J. Chem.*, **47**, 2306 (1969); (b) T. P. Lewis, *Tetrahedron*, **25**, 4117 (1969).

(13) R. G. Jesaitis and A. Streitwieser, Jr., *Theoret. Chim. Acta*, **17**, 165 (1970).

(14) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. "Standard geometries" were used; the calculations were carried out using the program CNINDO detailed in the book and obtained from Quantum Chemistry Program Exchange.

(15) A. Streitwieser, Jr., P. C. Mowery R. G. Jesaitis, J. R. Wright, P. H. Owens, and D. M. E. Reuben, "The Jerusalem Symposia on Quantum Chemistry and Biochemistry," Vol. II, The Israel Academy of Sciences and Humanities, 1970, p 160.

(16) (a) Alfred P. Sloan Fellow; (b) National Science Foundation Predoctoral Fellow, 1966–1970.

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A New Synthesis of Olefins

Sir:

We describe a new and general synthesis of tetrasubstituted olefins noteworthy for its simplicity and for producing pure products in high yields. Both symmetrical and unsymmetrical olefins are readily obtained.

In this synthesis aliphatic nitro compounds[1] are

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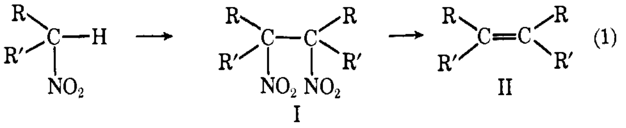
(1) These are readily available commercially, or by a variety of well worked out procedures: *cf.* N. Kornblum, *Org. React.*, **12**, 101 (1962).

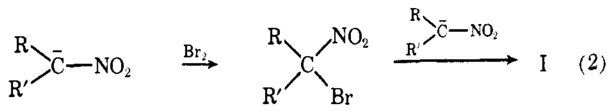
transformed into olefins by the sequence of eq 1. A


(1)

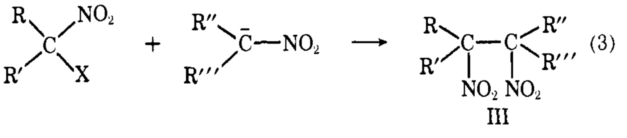
I

II

number of effective methods for converting aliphatic, and alicyclic, nitro compounds into vicinal dinitro compounds, I, are known;[2–4] the reaction originally described by Seigle, Hass, and Hudgin[2] has proved to be especially useful. When a nitroparaffin salt is treated with bromine in the cold it is rapidly and quantitatively converted to the α-bromonitro compound; this, without being purified, is treated with a second equivalent of the nitroparaffin salt whereupon the pure vicinal dinitro compound I is produced in 88–93% overall yield (eq 2).


(2)

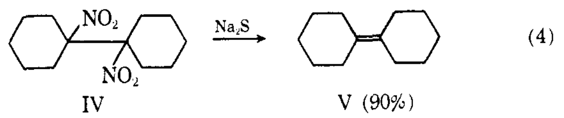
The preparation of unsymmetrical vicinal dinitro compounds by the corresponding reaction (eq 3; X = Br) is not satisfactory because, in addition to the desired compound III, substantial amounts of the two symmetrical vicinal dinitro compounds are produced.[5] However, by employing an α,α-dinitro compound in the reaction of eq 3 ($X = NO_2$),[6] 86–91% yields of


(3)

III

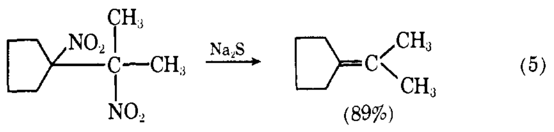
pure, unsymmetrical vicinal dinitro compounds, III, are obtained.[4]

The novelty of our olefin synthesis resides in the second step of eq 1. The conversion of vicinal dinitro compounds into olefins occurs smoothly when a solution of the dinitro compound in DMF is treated with sodium sulfide;[7] eq 4 and 5 are illustrative. The


(4)

IV

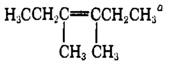
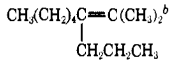
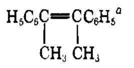
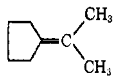
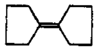
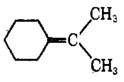
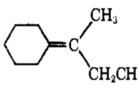
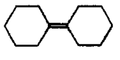
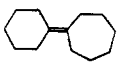
V (90%)


(5)

(89%)

generality of this reaction is evident from the results summarized in Table I; the merit of the olefin synthesis becomes especially clear when it is recognized that the yields of olefins refer to pure, isolated products.[8]

Table I. Olefins Synthesized from Vicinal Dinitro Compounds

Olefin	% yield
 $H_3CCH_2\underset{CH_3}{C}{=}\underset{CH_3}{C}CH_2CH_3$[a]	82
 $CH_3(CH_2)_4\underset{CH_2CH_2CH_3}{C}{=}C(CH_3)_2$[b]	88
 $H_5C_6\underset{CH_3}{C}{=}\underset{CH_3}{C}C_6H_5$[a]	82
	89
	92
	90
	91
	90
	84

[a] No stereochemistry implied. [b] We thank Professor G. B. Bachman and Dr. R. J. Maleski for the 4-nitrononane used in this synthesis.

This new elimination process is noteworthy for producing olefins free of isomers. Thus, even though a double bond exocylic to a five-, six-, or seven-membered ring is prone to isomerize into the ring[9] this does not occur under the conditions of our reaction.

As a typical example, lithium methoxide, prepared by dissolving 0.69 g (0.1 g-atom) of lithium in 100 ml of methanol, is treated under nitrogen with 12.6 g (0.098 mol) of nitrocyclohexane.[10] After removal of the methanol, the lithium salt is dissolved in 50 ml of water, cooled, and treated with 15.98 g (0.1 mol) of bromine. The resulting oil is taken up in pentane, washed with water, and dried, and then the pentane is removed. The bromonitro compound in 50 ml of DMSO is added to 14.6 g (0.108 mol) of the lithium salt of nitrocyclohexane suspended in 150 ml of DMSO and the mixture is maintained (under nitrogen) at 20–25° for 2 hr. On pouring into water and recrystallizing from acetone, 22.25 g (89% yield) of the vicinal dinitro compound IV is obtained; mp 216–217°. Under nitrogen, a stirred mixture of IV (15.44 g; 0.06 mol) and $Na_2S \cdot 9H_2O$ (36 g; 0.15 mol) in 250 ml of DMF

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(2) L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940); D. E. Hudgin, M.S. Thesis, Purdue University, 1940.

(3) A. H. Pagano and H. Shechter, *J. Org. Chem.*, **35**, 295 (1970).

(4) N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Amer. Chem. Soc.*, **92**, 5783 (1970).

(5) We shall discuss this matter in the full paper.

(6) Fortunately, the requisite α,α-dinitro compounds are readily obtained in yields of the order of 90% by the excellent reaction discovered by R. B. Kaplan and H. Shechter (*J. Amer. Chem. Soc.*, **83**, 3535 (1961)). Professor Shechter has informed us that the amount of sodium nitrite given in his paper is incorrect; at least 1 mol should be used for each mole of nitroparaffin salt.

(7) Sodium thiophenoxide in HMPA is also very effective.

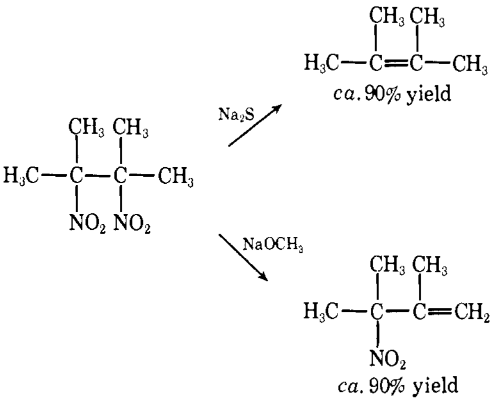
(8) Satisfactory elemental analyses and nmr and ir spectra were obtained for all new compounds.

(9) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Amer. Chem. Soc.*, **82**, 1750 (1960).

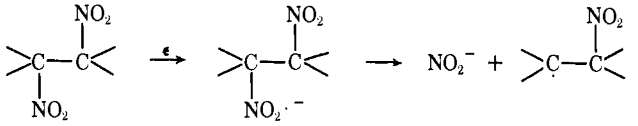
(10) We thank the Explosives Department of E. I. du Pont and Co. for a generous supply of nitrocyclohexane.

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.

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Received May 11, 1971

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

Sir:

The difficulties associated with effecting SN2 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

$$\begin{tikzcd}
\underset{\mathbf{1}}{R_1R_2C{=}NNHCO_2Me} \arrow[r, "HCN", "MeOH"'] & \underset{\mathbf{2}}{R_1R_2C(CN)NHNHCO_2Me} \arrow[d, "Br_2,\ aq\ NaHCO_3,\ CH_2Cl_2"] \\
 & \underset{\mathbf{3}}{R_1R_2C(CN)N{=}NCO_2Me}
\end{tikzcd}$$

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.