In the spectrum there appear to be three types of NF fluorines; two of these are coupled to form an AB or A_2B_2 group which is centered at -144 ϕ, and the third which is at -192 ϕ is apparently uncoupled. Two bands were observed in the SbF^7 region at 134 and 114 ϕ. A search for a more suitable media for obtaining the n.m.r. spectrum is underway.

Reaction of NF_2SbF_5 with species capable of being oxidized produced *trans*-N_2F_2 in about 90% yield. Several such reactions are

$$(C_5H_5)_2Fe + NF_2SbF_5 \xrightarrow[-45°]{SO_2} 0.5N_2F_2 + (C_5H_5)_2FeSbF_6$$

$$NOCl + NF_2SbF_5 \xrightarrow[-45°]{SO_2} 0.5N_2F_2 + 0.5Cl_2 + NOSbF_6$$

$$0.5I_2 + NF_2SbF_5 \xrightarrow[-45°]{SO_2} [I^+] + SbF_6^- + 0.5N_2F_2$$

These reactions could also be carried out in arsenic(III) fluoride at -6 to $-8°$ with similar yields. Characterization of the antimony species was performed in the first two cases only.

Acknowledgment. This work was performed under Army Ordnance Contract No. DA-01-021 ORD-11878.

(7) C. H. Hoffmann, B. E. Holder, and W. L. Jolly, *J. Phys. Chem.*, **62**, 364 (1958).

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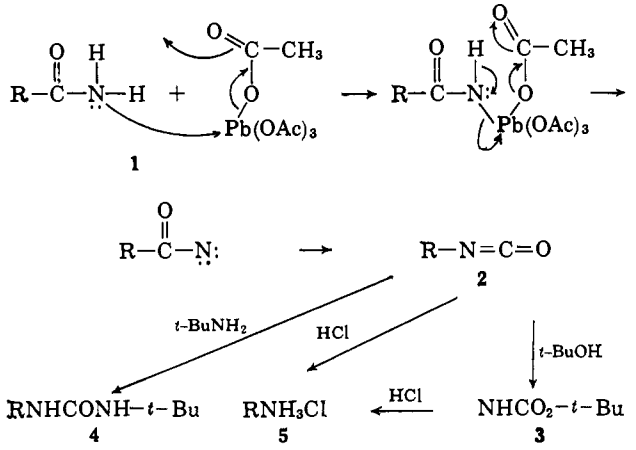
Reactions of Amines. XIV. An Oxidative Rearrangement of Amides[1,2]

Sir:

In an earlier communication[3] we reported an oxidative rearrangement of the N-amino amide, 1-aminooxindole, to 3-cinnolinol, a reaction presumably proceeding through a nitrene intermediate. More recently Campbell and Rees[4] have described the preparation of benzyne from 1-aminobenzotriazole *via* an oxidative elimination that also appears to proceed through a nitrene intermediate. In both of these reactions the oxidizing agent was lead tetraacetate.



(1) Paper XIII: *J. Org. Chem.*, in press.
(2) This work was supported in part by Public Health Service Research Grant CA-3090 from the National Cancer Institute.
(3) H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Am. Chem. Soc.*, **82**, 3977 (1960).
(4) C. D. Campbell and C. W. Rees, *Proc. Chem. Soc.*, 296 (1964).

We now report an oxidative rearrangement of simple amides using lead tetraacetate that yields products similar to those obtained from the Hofmann rearrangement.[5] Thus, under suitable reaction conditions[6] a number of aliphatic and aromatic amides could be quickly converted into the corresponding isocyanates **2** or their derivatives (**3**–**5**) in moderate to excellent yields. The mechanism shown is a greatly simplified one, reasonably consistent with the present understanding of lead tetraacetate oxidations[7] and our observations on this new reaction.

Simple aliphatic amides did not react appreciably with lead tetraacetate in acetic acid and reacted only sluggishly in nonpolar solvents such as benzene, chloroform, or methylene chloride. They reacted moderately rapidly in *t*-butyl alcohol and quite rapidly in this solvent in the presence of added triethylamine or, preferably, in dimethylformamide (without added base). These observations can be rationalized in part in terms of solvation effects and in part in terms of base catalysis, the base probably assisting in the removal of the proton in the second stage of the reaction. Aromatic amides were less reactive and reacted most satisfactorily in dimethylformamide with added triethylamine.

These reaction conditions were sufficiently vigorous to preclude the use of amides with functional groups capable of reacting with lead tetraacetate under milder conditions, *e.g.*, active methylene groups (phenylacetamide) and olefinic double bonds (cinnamamide).

When the reaction was run in *t*-butyl alcohol, the product isolated was the *t*-butylurethan **3**. The use of triethylamine in these reactions appeared to accelerate not only the oxidative rearrangement but also the reaction of the isocyanate with the alcohol, minimizing thereby the dehydration of the latter. Typical yields were; *t*-butyl-N-cyclohexylcarbamate,[8] m.p. 78–78.5°, 30% from cyclohexanecarboxamide; *t*-butyl-N-cyclobutylcarbamate,[8] m.p. 81°, 62% from cyclobutanecarboxamide; *t*-butyl carbanilate, m.p. 133–136° (lit.[9] m.p. 135–136°), 76% from benzamide; *t*-butyl *p*-chlorocarbanilate,[8] m.p. 105–106°, 71% from *p*-chlorobenzamide.

Methyl and ethyl alcohols could not be substituted for *t*-butyl alcohol for these alcohols reacted more rapidly with the reagent than did the amides.

Cleavage of the *t*-butylurethans with hydrogen chloride in ether proceeded rapidly to give high yields of the amine hydrochlorides **5**, *e.g.*, cyclohexylamine hydrochloride, 96%, cyclobutylamine hydrochloride, 79%, *p*-chloroaniline hydrochloride, 83%.

When the reaction was run in dimethylformamide, the isocyanate **2** could be isolated but isolation in most of the examples in this work was complicated by similarities in boiling point between product and solvent. For example, from the oxidative rearrangement of pivalamide a 44% yield of pure *t*-butyl isocyanate

(5) P. A. S. Smith, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1964.
(6) Amides, being less basic than N-amino amides, require more strenuous reaction conditions than N-amino amides.
(7) R. Criegee, "Newer Methods of Preparative Organic Chemistry," Vol. I, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1948, p. 16; Vol. II, p. 368, 1963.
(8) All products gave elemental analyses and infrared spectra compatible with assigned structures. Where solubility permitted, additional confirmation was obtained from n.m.r. spectra.
(9) E. Knoevenagel, *Ann.*, **343**, 46 (1905).

(less than half of the actual amount present) was recovered by simple fractional distillation, although a greater proportion could be recovered by gas chromatography. Thus in most experiments, the yield of isocyanate was estimated by adding an excess of *t*-butylamine to the reaction mixture and recovering the *t*-butylalkyl- or arylurea **4**. Typical yields were: N,N-di-*t*-butylurea, m.p. 240 ± 2° (lit.[10] m.p. 242–243°), 96% from pivalamide; N-*t*-butyl-N-(α-phenylbutyl)-urea,[8] m.p. 192–193°, 97% from α-methyl-α-phenylbutyramide; N-*t*-butyl-N-cyclohexylmethylurea,[8] m.p. 150–151°, 74% from cyclohexaneacetamide; N-*t*-butyl-N-cyclohexylurea, m.p. 226 ± 2° (lit.[11] m.p. 227°), 88% from cyclohexanecarboxamide.

The isocyanate could also be hydrolyzed directly to the amine hydrochloride **5** by adding the dimethylformamide solution to hydrochloric acid and heating the mixture under reflux. For example, from cyclocarboxamide a 49% yield of cyclohexylamine hydrochloride was obtained.

Typical procedures follow: to a mixture of 0.03 mole of amide, 0.03 mole of powdered lead tetraacetate, and 70 ml. of dry *t*-butyl alcohol warmed to 50–60° 10 ml. of triethylamine was added dropwise (*ca.* one drop every 3–4 sec.) with no additional heating. The initial reddish color of the mixture faded to white (or pale pink) within a few minutes. At this point conversion to the isocyanate was essentially complete and the remainder of the triethylamine could be added more quickly. The reaction mixture was allowed to stand for several days at room temperature during which time the disappearance of infrared band at *ca.* 2260 $cm.^{-1}$ could be used as a qualitative test for completeness of conversion to the urethan. The mixture was evaporated to *ca.* 30 ml. and poured onto crushed ice and 15 ml. of acetic acid. The urethan was collected, dried, and recrystallized from a hydrocarbon solvent.

To a stirred solution of 0.02 mole of amide in 100 ml. of dry, distilled dimethylformamide was added 0.02 mole of powdered lead tetraacetate. The addition caused the solution to become light red. As the reaction proceeded to completion the temperature rose to *ca.* 60°, and the color faded. (For aromatic amides, 5 ml. of triethylamine was added after the addition of lead tetraacetate.) When the solution was colorless again, 7 ml. of *t*-butylamine was added, and the disubstituted urea was precipitated by pouring the reaction mixture over 100 g. of crushed ice and water. The ureas could be recrystallized from ethanol.

The mechanism, scope, limitations, and extensions of this oxidative rearrangement are under study.

(10) B. Brauner, *Chem. Ber.*, **12**, 1875 (1879).
(11) R. N. Lacey, *J. Chem. Soc.*, 1633 (1960).

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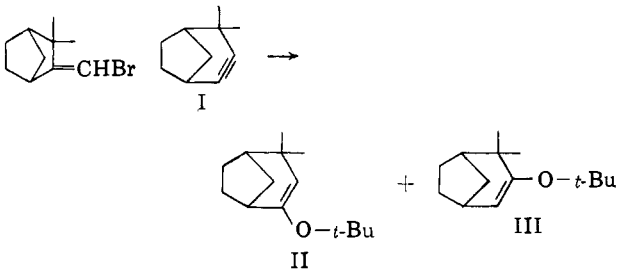
Rearrangement of Bromomethylenecycloalkanes with Potassium *t*-Butoxide

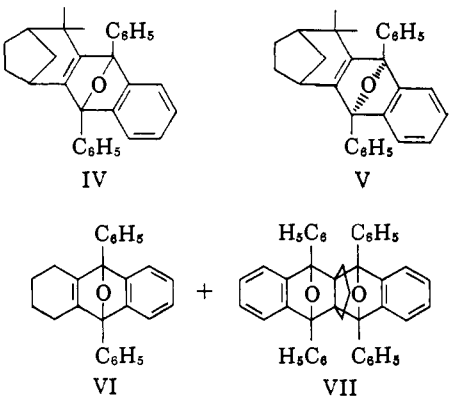
Sir:

Rearrangement of 2-bromo-1,1-disubstituted ethylenes to acetylenes has long been known in examples where the substituents are aromatic[1] and has recently been shown to occur where the substituents are aliphatic.[2] 1,2-Dibromo-2-methylpropane[2] or 1-bromo-2-methyl-1-propene,[3] on heating with potassium *t*-butoxide in nonpolar solvents, were converted into 2-butyne and 1-*t*-butoxy-2-methyl-1-propene,[3] and it was suggested that the vinyl ethers II and III obtained by heating ω-bromocamphene with potassium *t*-butoxide form by way of endocamphyne (I).[2] We now wish to report that the action of potassium *t*-butoxide on



bromomethylenecycloalkanes provides a useful, new method for generating highly strained cycloalkynes.[4]

When ω-bromocamphene (0.046 mole) was heated for 4 hr. with sublimed potassium *t*-butoxide (0.090 mole) and 1,3-diphenylisobenzofuran (0.046 mole) in toluene, there was obtained a 94% yield of a mixture of *exo* and *endo* adducts IV and V, m.p. 185–186° and 178–179°.[5]



Other strained cycloalkynes were generated by similar treatment of the appropriate bromomethylenecycloalkane[6] and were captured as 1,3-diphenylisobenzofuran adducts. Cyclohexyne, generated from bromomethylenecyclopentane, was trapped in 35% yield as the adduct VI, m.p. 170–171.5°, and cyclopentyne, produced from bromomethylenecyclobutane, was captured in 12.3% yield as a 1:2 adduct VII of unknown stereochemistry, m.p. 247–249°. This adduct was identical with a sample of VII kindly supplied by Professor G. Wittig.[7]

(1) *Cf.* W. M. Jones and R. Damico, *J. Am. Chem. Soc.*, **85**, 2273 (1963); W. Tadros, A. B. Sakla, M. S. Ishak, and E. R. Armanious, *J. Chem. Soc.*, 4218 (1963), and references cited therein.
(2) J. Wolinsky, *J. Org. Chem.*, **26**, 704 (1961).
(3) J. Privett, M. S. Thesis, Purdue University, 1962.
(4) Evidence for the transient existence of strained cycloalkynes has been provided by L. K. Montgomery and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 4750 (1960), and G. Wittig and A. Krebs, *Chem. Ber.*, **94**, 3260 (1961).
(5) Satisfactory elemental analyses and spectral data were obtained for all new compounds.
(6) The bromomethylenecycloalkenes used in this study were prepared by the decarboxylative debromination of α-bromo-1-bromocycloalkylacetic acids. The details of these preparations will be described in a forthcoming publication.