[CONTRIBUTION FROM THE RESEARCH CENTER OF THE ESCAMBIA CHEMICAL CORP., WILTON, CONN.]

Oxidation of Isobutylene with Dinitrogen Tetroxide

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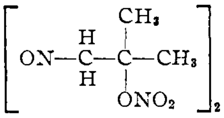
The reaction of isobutylene and dinitrogen tetroxide was studied. Good yields of the α-hydroxyisobutyric acid (69–74%) were obtained when isobutylene was added to excess dinitrogen tetroxide or to a nitric acid solution of dinitrogen tetroxide at about 0° and the resulting mixture was allowed to undergo oxidative and hydrolytic reactions. Attempts to determine the course of the reaction resulted in the isolation of α-nitratoisobutyraldehyde as an intermediate. Another intermediate, characterized by a strong infrared absorption at 6.45 μ, was detected but could not be isolated. This material spontaneously disappeared with the production of α-nitratoisobutyric anhydride. In the presence of nitric acid and water at 60° the aldehyde and anhydride were both converted to α-nitratoisobutyric acid and this was hydrolyzed under the same conditions to α-hydroxyisobutyric acid. The initial reaction of isobutylene and dinitrogen tetroxide is thought not to lead to nitro compounds under these conditions; rather the reaction probably involves nitrosonium nitrate and leads to isobutylene nitrosonitrate. The subsequent complex series of reactions leads to the aldehyde and anhydride.

The products of the reaction of dinitrogen tetroxide and isobutylene have been shown to be strongly influenced by the manner in which the reaction is carried out. When ethers or esters are used as solvents the reaction has been shown to proceed by a free radical mechanism[2,3] which leads to primary nitro compounds.[4] These include chiefly 1,2-dinitro-2-methylpropane (I), 1-nitro-2-nitrito-2-methylpropane (II), 1-nitro-2-methylpropan-2-ol (III), 1,3-dinitro-2-methylpropan-2-ol (IV) and 1-nitro-2-nitrato-2-methylpropane (V). The initial product is thought to result when $NO_2\cdot$ adds to the primary carbon atom, leaving an unshared electron on the tertiary carbon atom.[2] The resulting free radical can then react with another $NO_2\cdot$ to form either I or II. In the presence of oxygen the radical can probably form peroxy radicals which can lead to V by a sequence of steps involving further reaction with $NO_2\cdot$.[5]

However in the absence of ether or ester solvents the products are quite different, and nitro compounds are not formed. Distilling less than an equivalent of N_2O_4 into a petroleum ether solution of isobutylene at −10° results in an unidentified oil and a 12% yield of isobutylene nitrosonitrate dimer VI, along with unidentified oils.[6] When isobutylene was distilled into excess liquid dinitrogen tetroxide, a 22% yield of α-nitratoisobutyric acid resulted along with an unidentified oil corresponding to about 40% of the isobutylene.[4] It has recently been disclosed that yields of α-hydroxyisobutyric acid as high as 80% can result if isobutylene is allowed to react with N_2O_4 either alone or in nitric acid solution and the resulting product is subjected to hydrolytic and oxidative conditions.[7a,b]


$$\left[ON-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{ONO_2}{C}}-CH_3\right]_2$$
VI

Experimental[8]

General.—The initial reaction between isobutylene and dinitrogen tetroxide was carried out both batchwise and on a continuous basis with equivalent results. The continuous reactor was a 304-stainless steel cylindrical vessel 15 cm. deep, 4.7 cm. i.d. The vessel was jacketed and provided with a stirrer, thermocouple well and a liquid draw-off tube which maintained the liquid level 8 cm. above the bottom of the vessel. Both liquid and gaseous products were drawn off through this tube to a disengaging section which allowed the liquid phase to drop out and flow to a receiver. The vapors passed through a trap cooled with Dry Ice. The uncondensed gases were sampled for mass spectrometric analysis and measured in a wet test meter. The reaction temperature was controlled at 0 ± 0.5° by means of an electronic potentiometer which regulated the flow of chilled acetone through the reactor jacket. Isobutylene and dinitrogen tetroxide were metered as liquids in calibrated rotameters and were fed into the reaction chamber below the liquid level. The isobutylene was completely vaporized before entering the reactor and the reaction took place at atmospheric pressure. The initial reaction occurs virtually instantaneously and no unabsorbed isobutylene was observed to escape from the reactor. The feed rates and reaction conditions were held constant until the composition of the effluent showed no change with time and then long enough for a sample to be collected. The liquid product was collected in a glass flask immersed in Dry Ice.

At this stage the material is capable of undergoing a strongly exothermic reaction, but the rate of the reaction is slow at temperatures below about 20°. The mixture is then allowed to undergo this reaction by maintaining the temperature at 60° for 2 hours. Both hydrolytic and oxidative reactions occur during this interval leading eventually to the formation of α-hydroxyisobutyric acid.

All infrared spectra were measured on a Baird model 455 infrared spectrophotometer.

Nitric Acid Solvent.—The solution obtained by dissolving 600 g. of dinitrogen tetroxide in 3000 g. of 70% aqueous nitric acid was pumped into the stirred continuous reactor at a flow rate of 9.2 g./min. Isobutylene was added at 0.74 g./min. and the temperature was controlled at 5°. A 4-hour period was allowed for steady state conditions to be attained, after which the product was collected over a 100-minute interval. The product was heated to 30°, held at that temperature for 30 minutes, and then cooled to about 0° and stirred under a water-aspirator vacuum until the dark brown color began to lighten, indicating that most of the dinitrogen tetroxide and dinitrogen trioxide had been volatilized. A white precipitate was visible at this point. The suspension was cooled to incipient freezing of the solution and filtered through a sintered glass funnel. The wet solid weighed 72 g., and could be dissolved completely in 800 ml. of water. Upon cooling the material crystallized and was identified as α-nitratoisobutyric acid by its infrared spectrum.

Anal. Calcd. for $C_4H_7NO_5$: C, 32.2; H, 4.7; N, 9.4; acidity, 6.71 meq./g. Found: C, 32.5; H, 5.1; N, 8.9; acidity, 6.73, ester by saponification, 6.72 m.eq./g.

A carbon analysis by wet combustion of the aqueous solution of the α-nitratoisobutyric acid indicated that it had been obtained in 35% yield. The filtrate from which the

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[1] National Research Corp., Cambridge 42, Mass.

[2] H. Shechter and F. Conrad, THIS JOURNAL, **75**, 5610 (1953).

[3] J. C. D. Brand and I. D. R. Stevens, *J. Chem. Soc.*, 629 (1958).

[4] N. Levy, C. W. Scaife and A. E. Wilder-Smith, *ibid.*, 52 (1948).

[5] T. E. Stevens, THIS JOURNAL, **81**, 3593 (1959).

[6] A. Michael and G. H. Carlson, *J. Org. Chem.*, **5**, 1 (1940).

[7] (a) N. Robertson and T. R. Steadman, U. S. Patent 2,847,465 (1958); (b) J. H. Gardner and T. R. Steadman, U. S. Patent 2,847,453 (1958).

[8] Mixtures of dinitrogen tetroxide and many organic compounds are capable of undergoing violent explosions when detonated. Proper precautions should be observed with these systems.

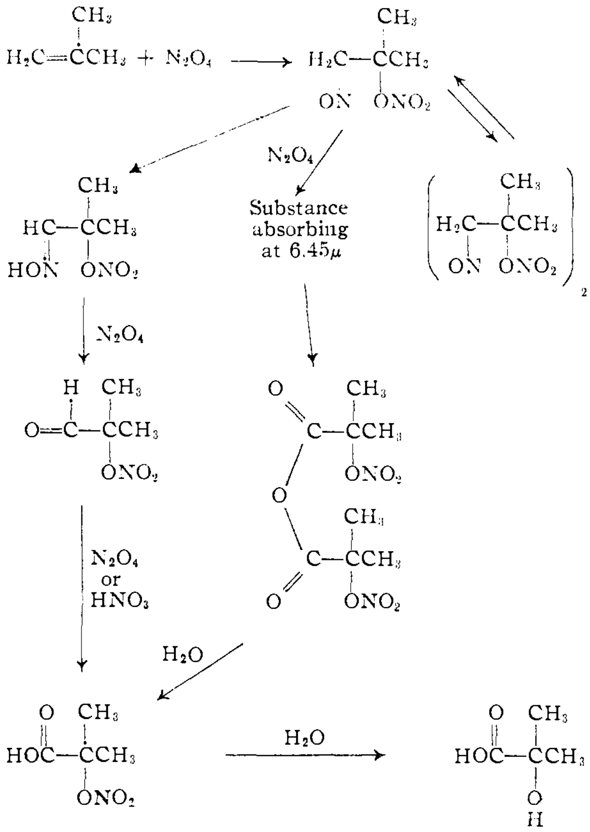

Fig. 1.—Oxidation of isobutylene with N_2O_4.

α-nitratoisobutyric acid had originally been obtained was concentrated by evaporation at about 0.5 mm. pressure and temperatures between 10 and 20° until 64.3 g. of pasty residue remained. This was dissolved in 100 ml. of hot benzene, cooled and filtered to yield 27.2 g. of white crystals identified as α-hydroxyisobutyric acid by infrared spectrum (acidity = 9.30 meq./g., theor. 9.61). The infrared spectrum of the filtrate, after evaporating the benzene under water-aspirator pressure, indicated it to be largely a mixture of α-nitratoisobutyric acid and α-hydroxyisobutyric acid. The mixture was hydrolyzed by dissolving in 380 ml. of 2 *N* sodium hydroxide solution and holding at 60° for 42 hours. It was then cooled in an ice-bath, acidified with 28 ml. of concd. sulfuric acid, and extracted continuously with ethyl ether for 2 days. The extract was dried with anhydrous magnesium sulfate and evaporated. The pasty residue was crystallized from benzene to yield 19.9 g. of white crystals of α-hydroxyisobutyric acid and 3.3 g. of oil which was not treated further. The α-hydroxyisobutyric acid was identified by its infrared spectrum; acidity = 9.65 meq./g. The total yield of α-hydroxyisobutyric acid was 34%. The yield of α-hydroxyisobutyric acid either as such or its nitrate ester was 69%.

Dinitrogen Tetroxide Solvent.—Dinitrogen tetroxide was pumped into the stirred reactor at 35.5 g./min. while isobutylene was metered through a rotameter at 2.98 g./min. The temperature was controlled at 0°. A sample was collected for a timed interval after steady state conditions had been attained. The nitrogen oxides were removed from the sample by distillation at about 20 mm. pressure, maintaining the temperature of the solution below 20°. Water was then added to the residue in an amount corresponding to two moles per mole of isobutylene fed to the reactor during the interval in which the sample was collected. The mixture was then held at 60° for 24 hours. This required cooling to remove the heat of reaction during the first hour and heating thereafter. The solution was then evaporated at room temperature and a pressure of 0.5 mm. to leave a solid residue which was characterized by its infrared spectrum as α-hydroxyisobutyric acid with small amounts of α-nitratoisobutyric acid as the principal impurity. The yield as calculated from the weak acid content of the crystals was 74%.

In similar runs it was demonstrated that the principal organic by-product is acetic acid. This acid was isolated from a sample of the distillate obtained after the hydrolysis treatment by partition chromatography, using aqueous silica gel as the stationary phase and a mixture of 0.66 volume of methylene chloride per volume of methyl ethyl ketone as the eluent. The acetic acid yield was 10%.

The fixed gases given off during the reaction are listed in Table I.

TABLE I

FIXED GASES FROM ISOBUTYLENE–N_2O_4 REACTION

	Mole/mole isobutylene	
	Init. reacn. at 0°	Holding period at 60°
CO	0.057	0.067
CO_2	.169	.223
N_2	.372	.152
N_2O	.006	.078

It should be mentioned that the initial mixture obtained by adding isobutylene to dinitrogen tetroxide can be detonated with a blasting cap to produce an extremely violent explosion. However, the mixture was handled in the laboratory and even pumped centrifugally without encountering any detonations.

α-Nitratoisobutyraldehyde.—A stirred-reactor run, similar to that of the preceding example, was carried out at 0° with an isobutylene flow rate of 2.05 g./min. and a dinitrogen tetroxide flow rate of 16.8 g./min. The nitrogen oxides were distilled off a sample of the steady-state reaction product under reduced pressure and a temperature between −10 and 0°. The residual oil was stirred with an excess of saturated aqueous sodium bicarbonate solution to neutralize the acidity and then washed from the aqueous solution with methylene chloride. A carbon analysis by combustion, performed on the oil after the methylene chloride had been removed by distillation at room temperature and reduced pressure showed it to contain 84% of the isobutylene carbon fed to the reactor during the interval in which the sample was collected. A carbonyl analysis, performed by hydrolyzing the nitrate esters in a sample of the oil in 0.5 *N* sodium hydroxide solution for 30 minutes on a steam bath and then treating the neutralized residue with hydroxylamine hydrochloride, showed 59% of the carbon in the oil to be present as an aldehyde (calculated as C_4). The aldehyde was isolated from the oil by vacuum distillation, coming over at 30° and 5 mm. pressure. The distillate was characterized as α-nitratoisobutyraldehyde by the analyses; infrared spectrum (in methylene chloride): major peaks at 5.78, 6.11, 7.22, 7.32, 7.74, 8.80, 11.10 and 11.76 μ.

Anal. Calcd. for $C_4H_7NO_4$: C, 36.1; H, 5.26; N, 10.5, functional group 7.5 meq./g. Found: C, 36.1; H, 5.0; N, 10.0; nitrate ester, 7.7 meq./g.; carbonyl, 7.1 meq. g.

α-Nitratoisobutyric Anhydride.—Reaction product obtained from the stirred reactor and freed of nitrogen oxides by distillation, as in the previous example, was held at 0° for 8 hours while under 1 mm. pressure. The infrared spectrum of the oil indicated the presence of α-nitratoisobutyraldehyde and of a compound absorbing at 5.47 μ. There was also a small absorption at 6.41 μ. The aldehyde was extracted from the mixture with aqueous sodium bisulfite, leaving a residue which was characterized as α-nitratoisobutyric anhydride by analyses: (There remained a small infrared absorption at 6.41 μ which is thought to be due to an impurity since (a) other fractions have been obtained in which this peak is quite large, and (b) the anhydride would not be expected to absorb at this wave length.)

When the material was dissolved in methanol its infrared spectrum gradually changed to that expected for an equimolar mixture of α-nitratoisobutyric acid and methyl α-nitratoisobutyrate; infrared spectrum (in methylene chloride): major peaks at 5.48, 5.68, 6.05, 6.11, 7.71, 8.68, 9.57 μ.

Anal. Calcd. for $C_8H_{12}N_2O_9$: C, 34.3; H, 4.3; N, 10.0; mole. wt., 280; nitrate ester, 7.1 meq./g.; sapon. 14.2 meq./g. Found: C, 34.6; H, 4.4; N, 10.3; mole. wt. (cryoscopically in benzene), 278; nitrate ester, 6.2 meq./g.; sapon. 12.8 meq./g.

Early Intermediates.—A modified reactor was constructed to enable the intermediate product to be examined before extensive secondary reaction had occurred. In this case the isobutylene was introduced axially into the upper end of a 30 mm. length of 0.25″ 304-stainless steel tubing with an i.d. of 4.57 mm. A 2.77-mm. o.d. thermocouple well placed axially in the reactor extended to within 6 mm. of the isobutylene inlet port, leaving an annular space of 0.9 mm. Dinitrogen tetroxide was introduced into an annulus above the isobutylene port. The reactants and the liquid and gaseous reaction products flowed downward through the annulus, while the heat of reaction was removed by flowing chilled acetone through a jacket surrounding the 0.25″ tubing.

At flow rates of 0.35 g./min. of isobutylene and 2.88 g./min. of dinitrogen tetroxide, measured in calibrated rotameters, and maintaining the coolant temperature at −25°, a peak temperature of 20° was measured at the isobutylene inlet. Temperatures downstream of the inlet rapidly approached that of the coolant. No unabsorbed isobutylene was found in the effluent gases. When a sample of the product of this reactor was worked up by the procedure described above in the section "Dinitrogen Tetroxide Solvent," a yield of 64% of α-hydroxyisobutyric acid was obtained.

An attempt was made to isolate the early reaction intermediates by passing the cooled effluent from the reactor directly to the top of a 90-cm. packed column, 2 cm. i.d. A countercurrent flow of air up through this column removed substantially all the nitrogen oxides overhead, leaving an oil as product. Washing the oil with ice-water to remove residual traces of nitrogen oxides and acids resulted in about 20% of the carbon content passing into the aqueous phase. The infrared spectrum of the oil showed the presence of α-nitratoisobutyric anhydride, as characterized by its absorption at 5.48 μ, α-nitratoisobutyraldehyde at 5.78 μ, nitrate ester at 6.11 μ and an unidentified compound absorbing at 6.45 μ. The oil was held at 40° and samples were removed at intervals for infrared examination in methylene chloride solvent. The absorbances of these samples calculated from the transmittances at the four above-mentioned wave lengths are presented in Table II. Within the limits of accuracy of the measurements those at 5.78 and 6.11 μ remained substantially constant during the interval. The 6.45 μ absorbance decreased and that at 5.48 μ increased proportionately. The material no longer showed the ability to self-heat at room temperature after the 6.45 μ absorbance had disappeared.

TABLE II

INFRARED ABSORBANCE OF EARLY INTERMEDIATE OIL AS A FUNCTION OF TIME AT 40°

	% of original absorbance			
	Wave lengths, μ			
Time, min.	5.48	5.78	6.11	6.45
0	100	100	100	100
5	130	100	100	71
15	150	99	91	53
34	163	100	95	40
72	173	75	94	0

The product obtained when the reactor effluent was run directly into a sodium bicarbonate solution and separated by decantation had an infrared spectrum similar to that obtained from the stripping column residue.

When a sample of the washed oil was dissolved in methylene chloride (3 wt. %) and the infrared absorbance at 6.45 μ was measured as a function of time at room temperature (about 25°), the absorbance was found to decrease at a first-order rate with a half-life of 40 minutes.

Materials.—Isobutylene, Matheson Co., Inc., C.P. Grade (99.0% min.); dinitrogen tetroxide, Matheson Co., Inc. (98.0% min.); nitric acid, Mallinckrodt A. R. (A.C.S.) (69–171%). All materials used as received without further purification.

Discussion

The marked effect of ethers in altering the products of the reaction has been attributed to a moderation of the oxidizing action of dinitrogen tetroxide through the formation of molecular addition compounds with these weakly basic solvents.[9,10] However, consideration of the results reported here indicates rather that two entirely different modes of reaction occur. In the presence of the ether solvents the products are virtually all primary nitro compounds. In the absence of these solvents the products can all be regarded as derivatives of isobutylene nitrosonitrate. We have found that primary nitro compounds are relatively stable to further reaction with either dinitrogen tetroxide or dinitrogen trioxide under the conditions of the addition reaction, and had they been formed, they would have been found in the product from the rapid reaction carried out in a tubular reactor, which allowed a contact time of only a few seconds. On the other hand, isobutylene nitrosonitrate is not found when ethers are used as solvent, nor can the observed products be derived from it under the reaction conditions. We therefore propose that the nitrosonitrate is the initial product when weakly basic solvents are not used.

The route by which the nitrosonitrate arises could be *via* the interaction of the olefin with dinitrogen tetroxide acting either as a molecule, ion-pair, or as dissociated ions, and conceivably all three routes are operative. In nitric acid solution, dinitrogen tetroxide is largely dissociated into nitrosonium and nitrate ions[11] and reaction *via* these species becomes an attractive hypothesis. In pure dinitrogen tetroxide the dielectric constant is too low to allow for dissociation but ion pairs have been estimated to exist to the extent of 0.001 mole fraction.[12] This concentration is likely considerably higher in ordinary dinitrogen tetroxide containing traces of water or of reaction products, and it is thought not unlikely that even in the case where the reaction is carried out in pure dinitrogen tetroxide that the reaction is *via* these ions. Many of the reactions of liquid N_2O_4 demonstrate its ability to react as NO^+ and NO_3^-.[13] For example, a detailed study of the reaction of metallic zinc with liquid dinitrogen tetroxide has led to the conclusion that below 14° the reaction occurs *via* nitrosonium nitrate acting as an ion pair.[14] It is therefore probable that the reaction leading to isobutylene nitrosonium nitrate also proceeds *via* ions. We do not consider that the facts at hand eliminate the possibility that the reaction is *via* direct addition of the N_2O_4 molecule to the olefin, but consider the ionic interaction more likely.

Isobutylene nitrosonitrate has not been isolated or identified as such, owing to its great reactivity. It dimerizes readily, however, and the isolation of the dimer by us and others is part of the evidence for the transitory existence of the monomer. Any unassociated monomer would isomerize to form the corresponding oxime. However, in the presence of excess dinitrogen tetroxide the oxime reacts rapidly to form the corresponding aldehyde. Thus Russian workers[15] have obtained a 93% yield of benzaldehyde from benzaldoxime and excess dinitrogen

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[9] B. Rubin, H. H. Sisler and H. Shechter, THIS JOURNAL, **74**, 877 (1952).

[10] N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1093 (1946).

[11] S. Lynn, D. M. Mason and W. H. Corcoran, *J. Phys. Chem.*, **59**, 238 (1955).

[12] C. C. Addison, N. C. Bolton and J. Lewis, *J. Chem. Soc.*, 1294 (1951).

[13] P. Grey and A. D. Yoffe, *Chem. Revs.*, **55**, 1069 (1955).

[14] C. C. Addison and J. Lewis, *J. Chem. Soc.*, 2833 (1951).

[15] S. S. Novikov, L. I. Khmel'nitskii and O. V. Lebedev, *Zhur. Obschei Khim.*, **28**, No. 8, 2296 (1958).

tetroxide. The reaction is rapid and exothermic and produces nitrogen as well as nitric oxide. This reaction is probably one source of the nitrogen gas which is found as a reaction product in the isobutylene reaction. The aldehyde is rather more stable, permitting it to be isolated if desired. When held at 60° for about an hour in the presence of nitric acid, the aldehyde is oxidized to the acid.

Another reaction intermediate is a compound having an infrared absorption at 6.45 μ. This was detected in the oil obtained from the tubular reactor, but the compound itself could not be isolated. It disappeared at a first-order rate from the neutral oil, as detected by changes in the infrared spectrum. The only major change observed in the infrared spectrum, other than the disappearance of the 6.45 μ absorption, was a corresponding increase at 5.48 μ, where α-nitratoisobutyric anhydride absorbs. Thus the 6.45 μ band is thought to be an intermediate in the formation of the anhydride. Absorption at 6.45 μ is characteristic of nitro or nitroso groups,[16] indicating that the compound contains nitrogen–oxygen bonds, but little else is known of its nature. No anhydride could be found in the N_2O_4 oxidation products of isobutyraldoxime or of α-nitratoisobutyraldehyde, and it is therefore suspected that the 6.45 μ absorbing material occurs from a reaction of N_2O_4 with isobutylene nitrosonitrate in a reaction that is competitive with isomerization to the oxime. The relation of these reactions is shown in Fig. 1.

Acknowledgments.—Elizabeth McElhill, Charles E. Dills and John O. H. Peterson contributed to the experimental work reported here.

(16) John F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Alkylation of Amines with *t*-Acetylenic Chlorides. Preparation of Sterically Hindered Amines[1]

BY G. F. HENNION AND ROBERT S. HANZEL[2]

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Aliphatic *prim-* and *sec*-amines are alkylated slowly at room temperature, in good yield, by *t*-acetylenic chlorides. The reaction is catalyzed by cuprous chloride. Catalysis is needed only in the case of aromatic amines; otherwise the latter react poorly. Many of the acetylenic amines produced have been hydrogenated to the corresponding allylic and saturated derivatives. A large number of new sterically hindered amines are described.

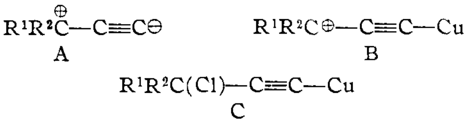
Discussion

The successful alkylation of *prim-* and *sec*-amines by *t*-acetylenic chlorides was first reported in a previous paper in this series.[3] The present study was undertaken to determine if this reaction is applicable to amines RNH_2 and $RR'NH$ of varied basicities and steric features; if the acetylenic amines, $R^1R^2C(NR^3R^4)C\equiv CH$, so produced are amenable to semi- and full hydrogenation without hydrogenolysis; and thus to ascertain if a new general route to sterically hindered amines of various types is available.

The simple reaction involved, namely

$$R^1R^2C(Cl)C\equiv CH + 2R^3R^4NH \longrightarrow R^1R^2C(NR^3R^4)C\equiv CH + R^3R^4NH\cdot HCl$$

succeeded in all cases studied and thus appears to be notably insensitive to steric features, except for rate. Thus *t*-butylamine, morpholine and piperidine reacted substantially as well as did ethylamine and *n*-propylamine. While an excess of R^3R^4NH ordinarily was used to serve as the HCl acceptor, triethylamine, potassium carbonate and potassium hydroxide often served equally well for this purpose, permitting use of R^3R^4NH in minimum amounts. In view of the mechanism previously proposed[3,4] for the reaction, it was surprising to observe that it is catalyzed by copper and by cuprous salts. When the amine subjected to alkylation was a strong base, catalysis ordinarily was not needed. With weakly basic compounds (aromatic amines) cuprous salt catalysis was necessary in order to obtain the products in good yields within a reasonable reaction time. While the mechanistic role of cuprous salts is not known, it may be that the dipolar ion intermediate[3,4] A is made more reactive in the form of the acetylide structure B. Alternatively, the *t*-acetylenic chloride used may form its acetylide C in the alkaline reaction mixture, subsequently leading to B and/or A as the species responsible for alkylation.



$$R^1R^2\overset{\oplus}{C}{-}C\equiv C^{\ominus} \qquad R^1R^2C^{\oplus}{-}C\equiv C{-}Cu \qquad R^1R^2C(Cl){-}C\equiv C{-}Cu$$

A B C

That elimination of HCl from the *t*-acetylenic chloride with formation of an eneyne hydrocarbon intermediate and subsequent addition of amine to the latter is not involved in the reaction mechanism was clearly shown by the fact that amines did not react with isopropenylacetylene, $CH_2{=}C(CH_3)C\equiv CH$, under any of the conditions which succeeded when chlorides were used.

Catalytic hydrogenation of the new compounds $R^1R^2C(NHR^3)C\equiv CH$ readily afforded the corresponding allylic and saturated derivatives ($-CH{=}CH_2$ and $-CH_2CH_3$, respectively, in place of $-C\equiv CH$). Semi-hydrogenation was achieved with either 5% $Pd/BaCO_3$ or 10% Pd/C in petroleum

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(1) Paper no. 71 on substituted acetylenes; previous paper, G. F. Hennion and F. X. O'Shea, *J. Org. Chem.*, **23**, 662 (1958).

(2) Eli Lilly Co. Fellow, 1957–1959. Abstracted from a portion of the Ph.D. Dissertation of R.S.H.

(3) G. F. Hennion and K. W. Nelson, THIS JOURNAL, **79**, 2142 (1957).

(4) G. F. Hennion, *et al.*, *ibid.*, **73**, 4735 (1951); **75**, 1653 (1953).