alcohol[15a] (above) and chloride[15a] (above) showed these substances to be absent, as was 2-methyl-3-phenylbutane[15b] (above). The crude hydrocarbon product had a spectrum that was a simple composite of that of neopentylbenzene and 2-methyl-3-phenyl-2-butene. For this reason it seemed safe to analyze the rectification fractions by refractive index (below). On this basis, the reduction product in this experiment contained a total of 13.3 g. (45%) of neopentylbenzene and 11.4 g. (39%) of 2-methyl-3-phenyl-2-butene.

In a similar experiment, in which fresh acid was added only when new zinc amalgam was put in, the yields were 30% of neopentylbenzene and 30% of the olefin.

When the reduction was carried out as above, changing only the amount of ketone (8.0 g., 0.5 mole) and using 160 ml. of methanol instead of water, there was obtained 3 g., b.p. 60° (10 mm.), $n^{20}D$ 1.5079. This value corresponds to 43% neopentylbenzene (17% yield) and 57% of the olefin (23%).

Clemmensen Reduction of *t*-Butylphenylcarbinol.—*t*-Butylphenylcarbinol (8.0 g., 0.05 mole) was reduced in aqueous methanol under the conditions described immediately above. There was obtained 4 g. of hydrocarbon, b.p. 70° (18 mm.), $n^{20}D$ 1.5141. The infrared spectrum showed the product to consist mainly of the olefin together with a small amount of neopentylbenzene. The refractive index corresponds to 24% (14% yield) neopentylbenzene and 76% (42% yield) of the olefin.

When this reduction was carried out using only water as a solvent there was obtained 4 g., b.p. 55–60° (10 mm.), $n^{20}D$ 1.5171, corresponding to 15% (5% yield) neopentylbenzene and 85% (26% yield) of the olefin.

A sample of 2-methyl-3-phenyl-2-butene was subjected to the conditions described immediately above. The infrared spectrum of the recovered hydrocarbon gave no evidence for the presence of neopentylbenzene.

Analysis of Hydrocarbon Mixtures by Refractive Index.—Mixtures of freshly distilled 2-methyl-3-phenyl-2-butene and neopentylbenzene were prepared. The refractive index *vs. weight* % olefin curve was a straight line.

Olefin, wt. %	$n^{20}D$	Olefin, wt. %	$n^{20}D$
0	1.4890	54.22	1.5066
16.94	1.4947	77.40	1.5142
25.84	1.4978	100.00	1.5221

W. LAFAYETTE, INDIANA

[CONTRIBUTION FROM DEFENCE RESEARCH CHEMICAL LABORATORIES AND CANADIAN ARMAMENT RESEARCH AND DEVELOPMENT ESTABLISHMENT]

The Structures of Nitroguanidine, 2-nitriminoimidazolidine and 1-Nitro-2-nitriminoimidazolidine[1]

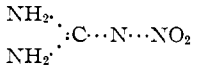
BY A. F. MCKAY, M. A. WEINBERGER, J. P. PICARD, W. G. HATTON, M. BEDARD AND H. E. ROONEY

RECEIVED MARCH 10, 1954

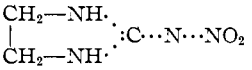
The behavior in alkaline solution of 1-nitro-2-nitriminoimidazolidine and 2-nitriminoimidazolidine has been investigated. It is shown that evidence from potentiometric titrations and methylation studies of these compounds is an unreliable guide to their structure.

Introduction

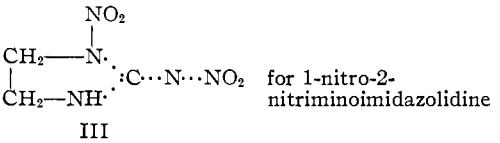
There have been several attempts described in the literature to clarify the structure of nitroguanidine and related compounds. McKay, Picard and Brunet[2] on the basis of ultraviolet spectra regarded nitroguanidine as a resonance hybrid to which forms with charge separation make a considerable contribution. On the other hand, Wright, *et al.*,[3,4] on the evidence of potentiometric titrations and methylation studies of these compounds assigned a simple nitrimine structure to them. Finally, Kumler[5] and Kumler and Sah[6] on the basis of dipole moment and acid strength measurements concluded that the above compounds are probably resonance hybrids with, however, only small contributions from forms with separation of charge. All authors are agreed that the basic nuclear skeleton is the symmetrical one



I, for nitroguanidine



II, for 2-nitriminoimidazolidine



III, for 1-nitro-2-nitriminoimidazolidine

In view of this agreement the present authors concede that structures such as II and III should be named nitrimines in the absence of a better term for the actual structures which in their view are resonance hybrids. This reverses the previous stand of McKay, *et al.*,[2] of using the classical names (*e.g.*, 2-nitramino-2-imidazoline for II). The traditional names give an erroneous description of the atomic skeleton and have led to confusion and to some quite undeserved criticism of the authors.[4]

It is realized that the final proof of the structure of nitroguanidine and related compounds will probably be given by crystal structure analysis. However, it is the purpose of the present paper to show that the evidence as to structure obtained from potentiometric titrations and methylation of these compounds is unreliable, and as regards the former to present chemical evidence for the complexity of the behavior of these compounds in alkaline solution.

The discussion concerning the structures of nitroguanidine, 2-nitriminoimidazolidine and 1-nitro-2-nitriminoimidazolidine will be confined to the last two compounds as there is general agreement that the structures of the first two are similar.

(1) Issued as D.R.C.L. Report No. 118.

(2) A. F. McKay, J. P. Picard and P. E. Brunet, *Can. J. Chem.*, **29**, 746 (1951).

(3) S. S. Barton, R. H. Hall and G. F. Wright, THIS JOURNAL, **73**, 2201 (1951).

(4) M. W. Kirkwood and G. F. Wright, *J. Org. Chem.*, **18**, 629 (1953).

(5) W. D. Kumler, *ibid.*, **18**, 676 (1953).

(6) W. D. Kumler and P. P. T. Sah, *ibid.*, **18**, 669 (1953).

Results

The behavior of 1-nitro-2-nitriminoimidazolidine and 2-nitriminoimidazolidine in alkaline solution was investigated spectroscopically. The products of alkaline hydrolysis of the former were also examined.

Figure 1 depicts the effect of time on the absorption spectrum of a 1 *N* potassium hydroxide solution of 1-nitro-2-nitriminoimidazolidine. The absorption spectrum taken immediately after the solution of the compound in the alkaline solution (curve A, Fig. 1) gives a curve with similar absorption characteristics to that in aqueous solution.

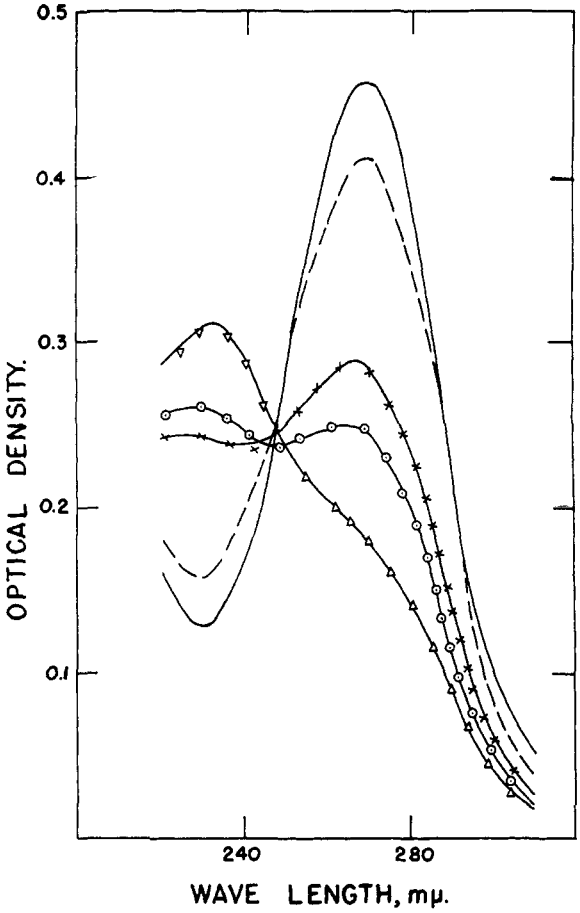
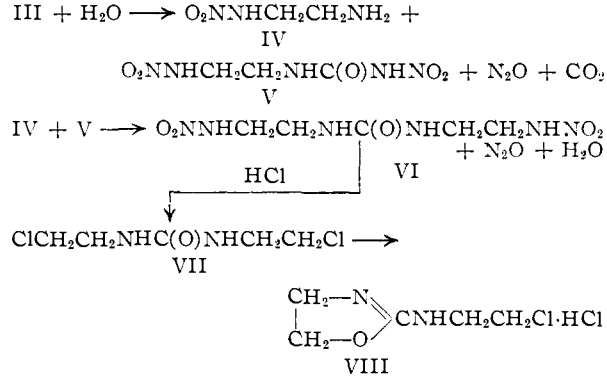


Fig. 1.—Curve A, fresh solutions of 1-nitro-2-nitriminoimidazolidine in *N* KOH, ——; curve B, same solution after 4 hours, — —; curve C, solution after 24 hours, ×—×; curve D, solution after 31 hours, ⊙—⊙; curve E, solution after 48 hours, Δ—Δ.

Figure 1 also shows that the optical density of the alkaline solution of the nitro compound begins to decrease immediately and that this continues with time. After 24 hours the absorption curve was the same as the absorption curve of 1β-nitraminoethyl-3-nitrourea (V) (*cf.* curve B, Fig. 1, ref. 7). 1-β-Nitraminoethyl-3-nitrourea has been isolated from the alkaline hydrolysis products of 1-nitro-2-nitriminoimidazolidine.[4] At the end of 48 hours the absorption of the alkaline solution indicated the presence of a primary nitramine which would be expected to be 1-amino-2-nitraminoethane (IV). The last compound also has been isolated from the hydrolysis products of 1-nitro-2-nitriminoimidazolidine.

When 1-nitro-2-nitriminoimidazolidine is refluxed in water, 1-amino-2-nitraminoethane (IV) and bis-(β-nitraminoethyl)-urea (VI) are formed. Bis-(β-nitraminoethyl)-urea was identified further by its conversion to the known bis-(β-chloroethyl)-urea[8] (VII) on standing in concentrated hydrochloric acid. If, however, bis-(β-nitraminoethyl)-urea is refluxed with concentrated hydrochloric acid solution, then 2β-chloroethylamino-2-oxazolinium chloride (VIII) (or its tautomer, 2β-chloroethyliminooxazolidine hydrochloride) is formed.

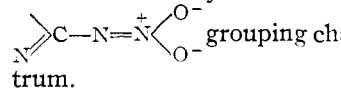


1-Nitro-2-nitriminoimidazolidine also is unstable in acid solution. In dilute hydrochloric acid solution ring opening occurs to give 1β-nitraminoethyl-3-nitrourea. The primary nitramino group is more susceptible to attack by acid than the nitrourea group and gives rise to the formation of 1β-chloroethyl-3-nitrourea. The final product of acid hydrolysis is β-chloroethylamine hydrochloride.

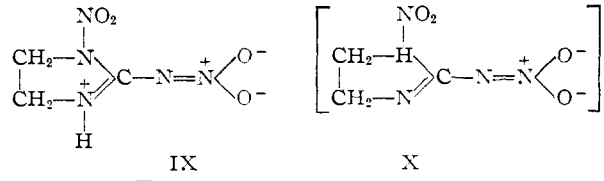
Figure 2 shows the changes in absorption spectrum of an alkaline solution of 2-nitriminoimidazolidine with time and it indicates that 2-nitriminoimidazolidine also disappears readily in alkaline solution. Quantitative studies[9] on the rate of hydrolysis of 2-nitriminoimidazolidine are in progress.

Discussion

As was seen above, the absorption curve of a freshly prepared alkaline solution of 1-nitro-2-nitriminoimidazolidine was similar to that of an aqueous solution. This would only be expected if the compound was a resonance hybrid with contributions from structures such as IX as the ion is almost certainly X. Both structures contain the



grouping characteristic of the spectrum.



(7) A. F. McKay and C. Sandorfy, *Can. J. Chem.*, **31**, 42 (1953).

(8) H. Bestian, *Ann.*, **566**, 210 (1950).

(9) M. A. Weinberger and A. F. McKay, in preparation.

The complicated chemistry of the subsequent hydrolysis of this compound in alkaline solution would vitiate the interpretation of its potentiometric titration curve as carried out by Wright, *et al.*[3] The latter authors were themselves misled by the potentiometric titration curves and assigned a nitramino structure to 1-nitro-2-nitriminoimidazolidine, in spite of the fact that it could be prepared in good yield by sulfuric–nitric acid nitration of 2-nitriminoimidazolidine.[10] This is in contradiction to their statement in the same paper that primary nitramines are unstable in this nitration medium. It is only recently that Kirkwood and Wright[4] have reversed their ideas and assigned a nitrimine structure to the compound. Again, previous to this, Wright[11] found by potentiometric titration that azo-bis-nitroformamidine was a dibasic acid. This fact was then set aside and a nitrimino structure tentatively assigned to it. It thus appears that potentiometric titrations are unreliable as guides to structure of these compounds.

The present authors[2] had not discussed the structure of 1-nitro-2-nitriminoimidazolidine in detail beyond implying that the compound was a resonance hybrid based on the nitrimine form. The substance was not regarded as a primary nitramine as erroneously quoted by Kirkwood and Wright,[4] although in conformity with common practice both the traditional name, 1-nitro-2-nitramino-2-imidazoline, and the corresponding formula was used when describing its reactions.

Kirkwood and Wright[4] attempted to prove the simple nitrimine structure of 1-nitro-2-nitriminoimidazolidine by evidence from methylation studies using diazomethane. Apart from the fact that the pure nitrimine structure presents no acidic hydrogen with which diazomethane may react, the products of methylation can be better explained in terms of a resonance hybrid structure involving contributions from structures such as IX. It is probable that during methylation the anion X plays an important part. This would account for the rather poor yield (19%) of 1-methyl-2-nitrimino-3-nitroimidazolidine and the production of an unidentified oil, probably an isonitramine.[4] Further evidence for the existence of this anion is provided by the formation of a beautifully crystalline silver salt when 1-nitro-2-nitriminoimidazolidine in aqueous solution is treated with silver nitrate solution.

The conclusion drawn by Barton, Hall and Wright[3] from potentiometric titration of alkaline solutions of 2-nitriminoimidazolidine that this compound is initially non-acidic and that it must therefore be a simple nitrimine is also erroneous. As was previously stated by the authors[2] for the very similar 2-nitrimino-(4 or 5)-methylimidazolidine and methylnitroguanidine there is an immediate formation of a different absorbing species when these compounds are dissolved in alkali. The same phenomenon has been found in the case of 2-nitriminoimidazolidine.[9] All these cases are complicated by the alkaline hydrolysis of the compounds as is indicated in Fig. 2 for 2-nitriminoimidazolidine.

(10) A. F. McKay and G. F. Wright, THIS JOURNAL, **70**, 3990 (1948).

(11) G. F. Wright, *Can. J. Chem.*, **30**, 62 (1952).

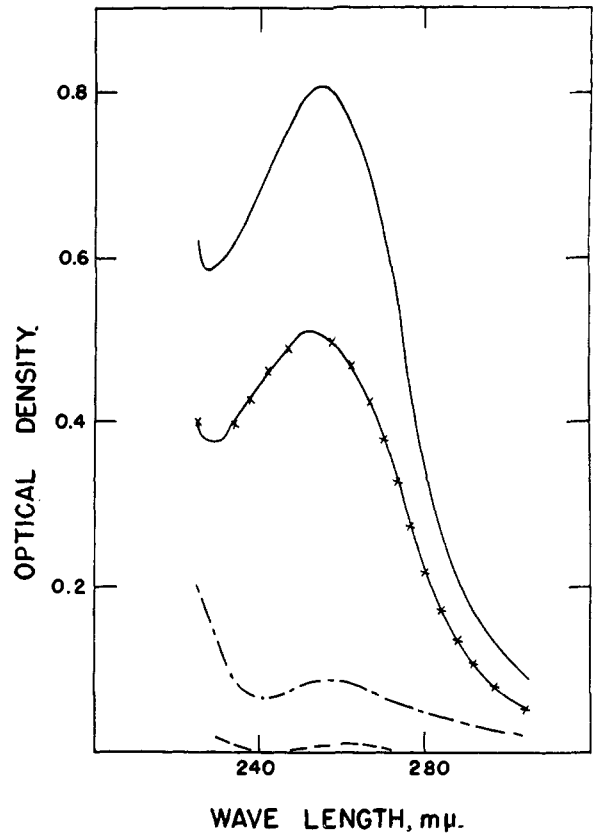


Fig. 2.—Curve A, fresh solution of 2-nitriminoimidazolidine in *N* KOH, ——; curve B, same solution after 4 hours, ×—×; curve C, solution after 24 hours, — - —; curve D, solution after 48 hours, — —.

Recently De Vries and Gantz[12] have determined the dissociation constants of nitroguanidine and related compounds and they too find the acidity function to appear instantaneously.

All this evidence counter-indicates the simple nitrimine structure, but would support the resonance hybrid structure for 2-nitriminoimidazolidine and nitroguanidine as previously suggested by the authors.[2]

Experimental[13]

1β-Nitraminoethyl-3-nitrourea.—1-Nitro-2-nitriminoimidazolidine (5 g., 0.028 mole) was dissolved in 25 cc. of 10% aqueous sodium hydroxide solution. After this solution had remained at room temperature for 46 hours it was carefully acidified at 2° with concentrated hydrochloric acid (4.0 cc.). The white solid (m.p. 100–103°) was filtered off and washed with cold water; yield 3.11 g. (56.4%). One crystallization from ethyl acetate raised the melting point to 104–105°.

Anal. Calcd. for $C_3H_7N_5O_5$: C, 18.65; H, 3.62; N, 36.24. Found: C, 18.62; H, 3.92; N, 36.04.

This compound gave a negative reaction with dimethylaniline in the Franchimont test while diethylaniline gave a pale green color.

Aqueous Hydrolysis of 1-Nitro-2-nitriminoimidazolidine.—1-Nitro-2-nitriminoimidazolidine (12 g., 0.068 mole) was refluxed in 30 cc. of water for 2.5 hours. The clear solution, on cooling in the refrigerator, deposited crystals which melted at 152.5° with decomposition; yield 4.47 g. (55.7%). The filtrate on evaporation to dryness gave 3.27 g. of solid;

(12) J. E. De Vries and E. St. C. Gantz, THIS JOURNAL, **76**, 1008 (1954).

(13) All melting points are uncorrected. Microanalyses by C. W. Beazley, Skokie, Ill.

total yield 7.74 g. (96.5%). This solid was extracted with hot ethanol which left behind an insoluble crystalline residue; yield 0.48 g. (6.67%). The decomposition point of this residue was raised from 223.9 to 230° by one crystallization from water. Several crystallizations from water were ineffective in increasing the decomposition point of this sample of 1-amino-2-nitraminoethane to the value of 240° reported by Hall and Wright.[14]

Anal. Calcd. for $C_2H_7N_3O_2$: C, 22.83; H, 6.66; N, 40.0. Found: C, 22.90; H, 6.72; N, 40.37.

The alcohol soluble crystalline product was purified by several crystallizations from ethanol and water. It melted at 160–161° with decomposition and gave analytical values in good agreement with bis-(β-nitraminoethyl)-urea.

Anal. Calcd. for $C_5H_{12}N_6O_5$: C, 25.41; H, 5.09; N, 35.57. Found: C, 26.01; H, 5.37; N, 35.25.

2β-Chloroethylamino-2-oxazolinium Picrate.—Bis-(β-nitraminoethyl)-urea (0.5 g., 0.002 mole) was refluxed with 10 cc. of 37% hydrochloric acid solution for 2.5 hours. The solution was evaporated to dryness and the oily residue (430 mg.) was redissolved in water (10 cc.). A picrate was formed in the usual manner, yield 445 mg. (55.6%). The melting point was raised from 184–187° to 193–194° by crystallization from water; yield 372 mg.

Anal. Calcd. for $C_{11}H_{12}ClN_5O_8$: C, 34.99; H, 3.18; N, 18.54. Found: C, 35.12; H, 2.95; N, 18.95.

Bis-(β-chloroethyl)-urea.—Bis-(β-nitraminoethyl)-urea (1.70 g., 0.072 mole) was dissolved in 8.0 cc. of concentrated hydrochloric acid. After the clear solution had remained at room temperature for six days, it was cooled to 20° and then it was carefully brought to a *p*H of 7 with 10% sodium hydroxide solution. The resulting mixture was cooled to 0° after which the white crystals were removed by filtration; yield 0.89 g. (67.3%). After one crystallization from absolute ethanol (7.9 cc./g.), the melting point was raised from 126.5–127° to 127–127.5°. Bestian[8] reports a melting point of 127° for bis-(β-chloroethyl)-urea.

Anal. Calcd. for $C_5H_{10}Cl_2N_2O$: C, 32.45; H, 5.42; Cl, 38.33; N, 15.15. Found: C, 32.67; H, 5.26; Cl, 38.00; N, 15.01.

Hydrolysis of 1-Nitro-2-nitriminoimidazolidine with Hydrochloric Acid.—Ten grams (0.057 mole) of 1-nitro-2-nitriminoimidazolidine was refluxed in 20 cc. of 20% hydrochloric acid solution until gassing ceased. The solution was concentrated to 10 cc. *in vacuo* after which crystals (m.p. 113–115°) were deposited on standing at room temperature; yield 1.27 g. (13.3%). After one crystallization from chloroform, these crystals melted at 117.5–119°. A mixed melting point determination with a sample of 1β-chloroethyl-3-nitrourea (m.p. 115–117°), kindly supplied by Dr. G. F. Wright, showed no depression.

The original filtrate was evaporated to dryness *in vacuo*. When attempts to crystallize the residual oil (5.89 g.) failed, it was dissolved in water (15 cc.) and treated with a saturated aqueous solution of picric acid and triethanolamine picrate. A yellow picrate was obtained in 19.4% yield (3.42 g.) which melted at 142–143°. This picrate did not depress the melting point of an authentic sample of β-chloroethylamine picrate (m.p. 143–144°).

Silver Salt of 1-Nitro-2-nitriminoimidazolidine.—An aqueous ethanol solution containing 1 g. of 1-nitro-2-nitriminoimidazolidine was treated with an aqueous ethanolic solution of silver nitrate. The crystalline silver salt, which formed immediately, was removed by filtration, washed and dried. It explodes when held on a spatula over an open flame.

Anal. Calcd. for $C_3H_4N_5O_4Ag$: Ag, 38.26. Found: Ag, 38.11, 38.29.

Ultraviolet Absorption Spectra.—The spectra were measured with a Beckman quartz spectrophotometer, model DU. Analytically pure samples were used to prepare the solution.

OTTAWA, ONTARIO, CANADA

(14) R. H. Hall and G. F. Wright, THIS JOURNAL, **73**, 2213 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

Mannich Bases of Nitroparaffins: Steric Effect of the Amino Groups on Carbon Alkylation

BY GRADUS L. SHOEMAKER AND ROBERT W. KEOWN

RECEIVED MARCH 25, 1954

Alkylations of active methylene compounds with the Mannich bases of nitroparaffins are shown to proceed more readily when the displaced amine has large bulky groups attached to it. The yields of the alkylation product in the reaction of the Mannich base of nitroethane with malonic, acetoacetic and acetylsuccinic esters doubled when piperidine was replaced by the more bulky diisopropylamine. In a similar manner alkylations of nitroparaffins with the diisopropylamino base were completed in a fraction of the time required for the more compact N-diethylamino-2-nitropropane.

The use of Mannich bases for carbon–carbon alkylation seems to require primarily that the tertiary Mannich base have the ability to form a conjugated unsaturated system through the displacement of the amino group.[1] The unsaturated compound thus formed then undergoes reaction with the active methylene compound by means of a Michael addition thus

$$\mathrm{RCHCH_2NR'_2} \xrightarrow[\mathrm{NO_2}]{} \xrightarrow{-\mathrm{R'_2NH}} \mathrm{RC{=}CH_2} \xrightarrow[\mathrm{NO_2}]{} \xrightarrow{+\ \mathrm{CH_2Z_2}} \mathrm{RCHCH_2CHZ_2} \xrightarrow[\mathrm{NO_2}]{}$$

The structural requirements of quaternary ammonium salts for use in similar alkylations (Robinson's method) are the same with the possible exception of those compounds which contain an allylic system attached to the nitrogen atom.[1] These allylic quaternary ammonium salts appear to be the only Mannich bases which can alkylate directly through a carbonium ion without the formation of an unsaturated intermediate.

Since then most carbon–carbon alkylations with Mannich bases proceed through this elimination–addition mechanism, it would appear that the more easily the amine is displaced from the Mannich base, the more readily would the unsaturated intermediate be formed. Ease of formation of this intermediate should then facilitate the subsequent addition reaction. Although numerous papers have considered the requirements for the alkylating radical in these alkylations, there have been few reports[1] concerning the effect of the displaced amino group. In particular it would seem that steric effects of bulky alkyl groups (F-strain) attached to the amino nitrogen would increase the ease of amine displacement from the Mannich

(1) J. H. Brewster and E. L. Eliel, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 99.