a solution of 1% hydrochloric acid in ethanol. The solvent was removed from the hydrazone solution on a flash evaporator and the residue was chromatographed on alumina to give 429 mg (82%) of acetone 2,4-dinitrophenylhydrazone (**24**), mp 123–125°, mmp 124–126°.

The basic solution was carefully acidified with hydrochloric acid and the precipitated **22** was collected by filtration, washed with water, and dried to yield 425 mg (66%) of pure **22**, mp 191–193°, mmp 190–191°.

E. 1-Chloro-*cis,trans*-2,3-dimethylaziridine (16). In a 50-ml round-bottomed flask equipped with a magnetic stirring bar and a distillation head was placed 25 ml of a 2.62×10^{-2} *M* solution of **16**. The solution was heated to reflux and the acetaldehyde which formed was distilled along with some water into 2,4-dinitrophenylhydrazine reagent. The precipitate which formed was collected by filtration and washed with a small amount of cold ethanol to give 190 mg (65%) of the 2,4-dinitrophenylhydrazone of acetaldehyde, mp 144.0–145.5° (lit.[26] mp 147°).

F. 1-Chloro-*trans,trans*-2,3-dimethylaziridine. (18). The same procedure as used for **16** was used for **18** to give 79% of the 2,4-dinitrophenylhydrazone of acetaldehyde.

(26) C. F. H. Allen, *J. Amer. Chem. Soc.*, **52**, 2955 (1930).

***cis*-2,3-Diphenylaziridine (32).** Desoxybenzoin oxime was converted into **32** by lithium aluminum hydride reduction according to the literature procedure.[27]

Reaction of 32 with Sodium Hypochlorite. A solution of 101 mg of **32** in 5 ml of tetrahydrofuran was stirred with 20 ml of 6% sodium hypochlorite solution (Purex) with a vibromix stirrer for 3 hr. The solution was extracted with pentane and the extracts were combined and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was evaporated under reduced pressure. The residue was dissolved in 10 ml of ethanol and 2,4-dinitrophenylhydrazone reagent was added to give 295 mg (53%) of benzaldehyde 2,4-dinitrophenylhydrazone, mp 237.5–238.0° (lit.[28] 237°).

Acknowledgment. The authors thank the National Cancer Institute of the Public Health Service for Grant No. CA-07110 which supported this work. We also thank Dr. David Dalrymple for stimulating discussions concerning this work.

(27) Patent to Shionogi and Co. Ltd., Netherlands Application 6,515,376; *Chem. Abstr.*, **65**, 15325a (1966); K. Kotera, S. Miyazaki, H. Takahashi, T. Okada, and K. Kitahonoki, *Tetrahedron*, **24**, 3681 (1968).

(28) F. L. Roduta and G. Quibilan, *Rev. Filipina Med. Farm.*, **27**, 123 (1936); *Chem. Abstr.*, **31**, 987 (1937).

The Reaction of Highly Strained Polycyclic Molecules with Carbon–Carbon Multiple Bonds[1]

Paul G. Gassman[2] and Gary D. Richmond[3]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received August 30, 1969*

Abstract: The addition of benzyne to tricyclo[4.1.0.$0^{2,7}$]heptane and the reaction of dicyanoacetylene with tricyclo[4.1.0.$0^{3,7}$]heptane have been studied in order to establish the stereochemical factors involved in the unusual addition of carbon–carbon multiple bonds to highly strained carbon–carbon single bonds. It was established that the attacking carbon–carbon multiple bond approaches the backside of the bent σ bond in an end-on manner. The specificity of the reaction is governed by the difference in steric environment of the two ends of the bent bond. The formation of 2-phenyltricyclo[4.1.0.$0^{3,7}$]heptane from the reaction of benzyne with tricyclo[4.1.0.$0^{2,7}$]heptane and the production of tricyclo[4.1.0.$0^{3,7}$]heptyl-5-maleonitrile from the addition of dicyanoacetylene to tricyclo-[4.1.0.$0^{3,7}$]heptane is discussed in terms of the intermediacy of a diradical species.

The addition of carbon–carbon double bonds to the strained σ bonds of small carbocyclic rings, which was first reported in 1965,[4,5] presented many interesting mechanistic questions. Although this reaction has been applied to a variety of systems,[6–9] it was only recently that the mechanistic details of this addition reaction have been clarified.[10–12] It has been demonstrated that the addition of olefins and acetylenes to bicyclo[2.1.0]pentane (**1**) occurs *via* the formation of a diradical intermediate[5,10,11] and that the approach of the carbon–carbon multiple bond is from the inside of the flap formed by the fused rings of bicyclo[2.1.0]-pentane.[12] The latter facet of the mechanistic picture was illustrated through the addition of maleic anhydride (**2**) to *exo,exo*-2,3-dideuteriobicyclo[2.1.0]pentane (**3**) to give **4** with the original label of **3** in the *exo* position of **4**. The stereochemistry of the deuterium labels of **4** required that the carbon–carbon multiple bond approach **3** from below the flap and invert the flap in the process of reacting.[11] This left, as the major unanswered mechanistic question, the problem of whether the carbon–carbon multiple bond approached the bottom side of **1** in a symmetrical manner as shown in **5**, or whether the approach was end-on as depicted by **6**. In order to demonstrate that a symmetrical ap-

(1) Paper XIII of a series on The Chemistry of Bent σ Bonds. For the preceding papers in this series see (a) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969) and (b) P. G. Gassman, F. J. Williams, and J. Seter, *ibid.*, **90**, 6893 (1968).

(2) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

(3) National Institutes of Health Predoctoral Fellow, 1965–1968.

(4) P. G. Gassman and K. T. Mansfield, *Chem. Commun.*, 391 (1965).

(5) A. Cairncross and E. P. Blanchard, Jr., *J. Amer. Chem. Soc.*, **88**, 496 (1966).

(6) C. D. Smith, *ibid.*, **88**, 4273 (1966).

(7) H. J. Reich and D. J. Cram, *ibid.*, **89**, 3078 (1967).

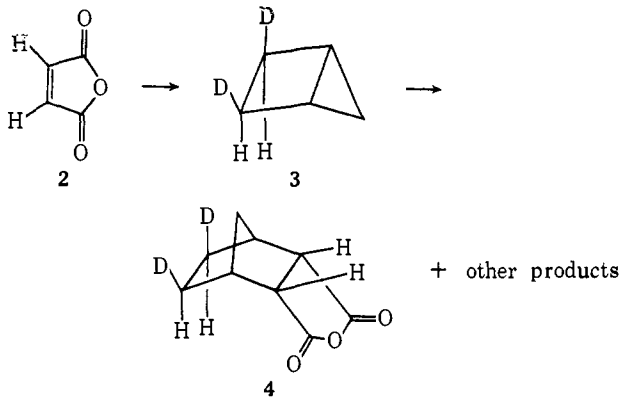
(8) M. R. Rifi, *ibid.*, **89**, 4442 (1967).

(9) M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968).

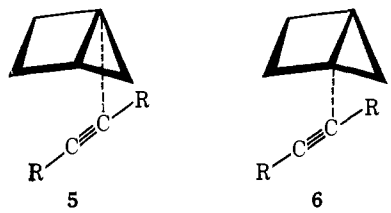
(10) P. G. Gassman and K. T. Mansfield, *ibid.*, **90**, 1524 (1968).

(11) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **90**, 4746 (1968); P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **91**, 1684 (1969).

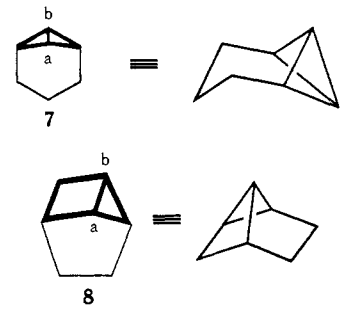
(12) It has been demonstrated that the approach of nitrogen–nitrogen double bonds also occurs from the inside of the flap of **1**: W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).



proach as shown in **5** was not a prerequisite for our reaction to occur, we investigated the reaction of carbon–carbon multiple bonds with strained polycyclic systems where symmetrical attack was sterically impossible. This paper presents the details of our investigation.[13]



In order to preclude a symmetrical approach to the backside of the bent σ bond of a highly strained fused-ring system, we studied cycloadditions to molecules in which the inside of the flap was protected by a methylene bridge. Ideal molecules for this study were **7**[14] and **8**.[15] In **7** we have a bicyclo[1.1.0]butane derivative in



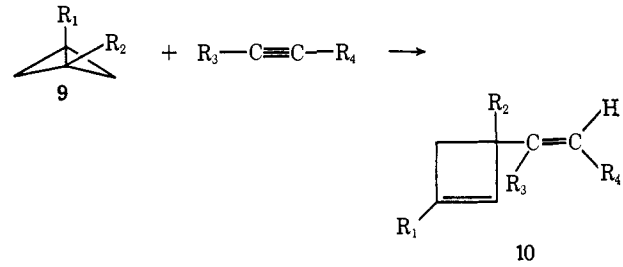
which the inside of the flap of the bicyclo[1.1.0]butane envelope is protected by a trimethylene bridge. This trimethylene bridge provides equal steric hindrance at positions a and b of **7**. The tricyclic, **8**, can be viewed as a bicyclo[2.1.0]pentane derivative in which the inside of the flap is protected sterically by an ethano bridge. It should be noted at this point that the ethano bridge in **8** provides greater hindrance at the a position than at the b position. Thus a study of additions to **8** not only permits a test of the mode of approach, but also allows an evaluation of the influence of slight differences in steric environment on the initial point of attack.

(13) For preliminary reports of part of this work see P. G. Gassman and G. D. Richmond, *J. Amer. Chem. Soc.*, 90, 5637 (1968); P. G. Gassman and G. D. Richmond, *Chem. Commun.*, 1630 (1968).

(14) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, 83, 2019 (1961).

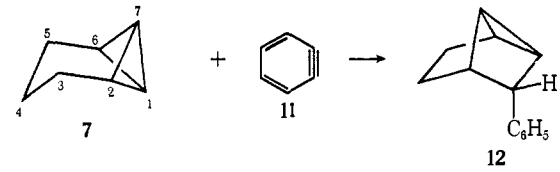
(15) H. C. Brown and H. M. Bell, *ibid.*, 85, 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, 85, 2324 (1963).

Our initial efforts in this study were involved with additions to tricyclo[4.1.0.0^{2,7}]heptane (**7**). In considering the bicyclo[1.1.0]butane derivative, **7**, it should be recalled that simple unbridged derivatives of bicyclo[1.1.0]butane (**9**) react with electron-deficient carbon–carbon multiple bonds to give primarily ene-type



products (**10**).[5,8,9,16] This type of ene reaction should not occur with **7** since this would require the formation of a double bond to the bridgehead of a bicyclo[3.1.1]heptane system in violation of Bredt's rule.[17]

When a slurry of 3 equiv of benzenediazonium-2-carboxylate[18] and 1 equiv of **7** was refluxed for 4 hr



in methylene chloride, a single product was obtained in 61% yield.[19] Mass spectral measurements showed a parent peak at *m/e* 170 which confirmed that the isolated material had been formed through the addition of 1 equiv of benzyne to 1 equiv of **7**. In addition to the parent peak (base peak) the mass spectrum showed an intense peak at *m/e* 91, corresponding to $C_7H_7^+$. The nmr spectrum of the adduct showed a five-proton singlet at τ 2.94, indicative of the presence of a monosubstituted benzene ring as part of the structure. This conclusion was substantiated by the infrared spectrum of the adduct which had bands at 13.80 and 14.40 μ and a pattern of absorptions in the 5.00–5.70-μ region characteristic of a monosubstituted benzene ring.[20] The large tropylium peak in the mass spectrum coupled with the nmr and infrared evidence for the presence of a monosubstituted benzene ring required that the benzyne abstract a hydrogen after its initial addition to the bent bond.

The near-infrared spectrum of the adduct had maxima at 1.657 and 1.673 μ characteristic of a strained cyclopropane C–H stretching overtone and an aryl C–H stretching overtone, respectively.[21] Additional spectroscopic evidence for the presence of a cyclopropane ring in **12** was provided by the upfield portion of the nmr spectrum. An absorption appearing as a quartet at τ 6.38 (1 H; J_{AB} = 4.0 cps, J_{AC} = 8.0 cps) was tentatively assigned to the benzylic proton. The

(16) P. G. Gassman and K. T. Mansfield, *ibid.*, 90, 1517 (1968).

(17) J. A. Marshall and H. Faubl, *ibid.*, 89, 5965 (1967); J. R. Wiseman, *ibid.*, 89, 5966 (1967).

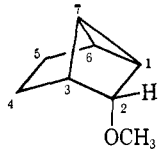
(18) L. Friedman and F. M. Logullo, *ibid.*, 85, 1549 (1963); L. Friedman, *ibid.*, 89, 3071 (1967).

(19) This material was shown to be *ca.* 97% pure by vpc.

(20) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 107 and 118.

(21) P. G. Gassman and W. M. Hooker, *J. Amer. Chem. Soc.*, 87, 1079 (1965).

rest of the spectrum consisted of a doublet with complex fine structure at τ 7.24 (1 H), a one-proton multiplet at τ 7.75, and a broad multiplet representing six protons in an envelope from τ 8.1 to 9.0. The aliphatic hydrogen portion of the nmr spectrum was very similar to that described by Tanida and coworkers for **13**.[22] These similarities in the nmr spectra indicated that the adduct was a derivative of tricyclo[4.1.0.0^{3,7}]heptane



13

with the phenyl group in the 2 position. Although the similarity of the nmr spectra and the large coupling constants[23] of the benzylic proton indicated that the phenyl group was *endo*, the spectroscopic evidence for the stereochemistry was not conclusive. Mechanistically, backside attack from inside the flap of the bicyclo[1.1.0]butane portion of **7** would give an *endo*-phenyl group, while frontside attack on the C_1–C_7 bond of **7** would give the phenyl an *exo* position (*vide post*).

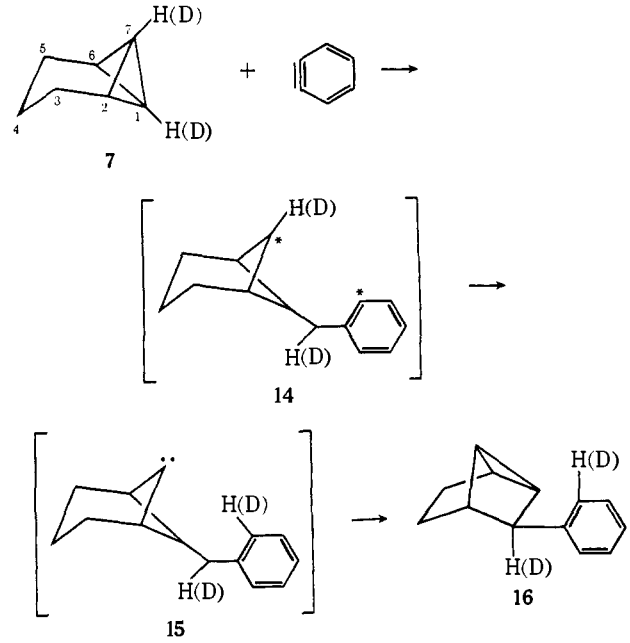
Chemical evidence for the presence of the tricyclo[4.1.0.0^{3,7}]heptyl moiety as part of **12** was provided by a combination of the rapid reaction of **12** with bromine in carbon tetrachloride and with hydrogen under catalytic conditions, coupled with the failure of **12** to react with either ozone or osmium tetroxide under conditions where olefins react rapidly. This type of chemical reactivity was identical with that found for tricyclo[4.1.0.0^{3,7}]heptane and its derivatives.[14,22,23]

Derivatives of tricyclo[4.1.0.0^{3,7}]heptane have been prepared *via* carbene insertion reactions[14] and carbonium ion trapping experiments.[15,22,23] In our system the formation of a carbene intermediate would require frontside attack by benzyne on **7** to give **14**. Transfer of the C-7 hydrogen would give the carbene **15**. Insertion of the carbene at either C-3 or C-5 would give **16**. As shown in Chart I, this hypothesis could be tested by placing deuterium in the 1 and 7 positions of **7** since the formation of a carbene would require transfer of the C-7 deuterium to the benzene ring. 1,7-Dideuteriotricyclo[4.1.0.0^{2,7}]heptane (**7**-d_2) was prepared according to the method of Closs.[24] When benzyne was added to **7**-d_2 no deuterium transfer occurred from C-7 to the benzene ring of **14**, as shown by the presence of five aromatic proton and seven aliphatic proton absorptions in the nmr of the product. Additional evidence for the lack of deuterium transfer to the benzene ring was provided by the mass spectrum of the deuterated product which showed that the major fragmentation product was $C_7H_6D^+$. If deuterium transfer had occurred this fragment would have been $C_7H_5D_2^+$.

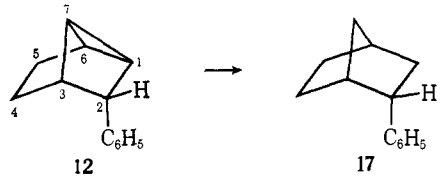
The possibility of frontside approach of the benzyne was eliminated completely by a study of the catalytic reduction of the adduct formed from benzyne and **7**.

(22) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **88**, 864 (1966).
(23) H. Tanida and Y. Hata, *J. Org. Chem.*, 30, 977 (1965).
(24) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963). Mass spectral analysis indicated that our sample of 7-d_2 contained in excess of 90% of two deuteriums.

Chart I



Tricyclo[4.1.0.0^{3,7}]heptane and its derivatives are known to suffer hydrogenolysis of the C_1–C_7 bond under



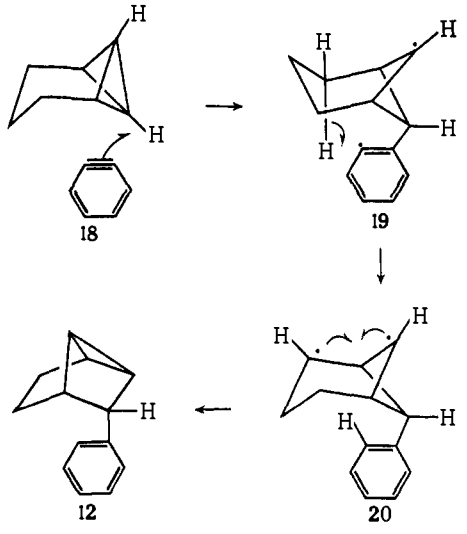
catalytic conditions to give derivatives of norbornane.[14,22,23] Thus, catalytic hydrogenation of our adduct over 5% Pd–C would give either *exo*- or *endo*-2-phenylnorbornane depending on the stereochemistry of the phenyl group in the adduct. This reduction gave only *endo*-2-phenylnorbornane[25] (**17**) which confirmed **12** as the structure of the adduct.

The stereochemistry of the phenyl group required that the benzyne attack the strained C_1–C_7 bond of **7** from the backside. Mechanistically, this could be explained in terms of either a thermal 2 + 2 + 2 concerted reaction[26] or the formation of a diradical intermediate. Definitive evidence for the formation of diradical intermediates in the addition of carbon–carbon multiple bonds to bicyclo[2.1.0]pentane provides ample precedent for the intermediacy of a diradical species in this reaction.[10,11] As shown in Chart II, the attack of benzyne on the inside of the flap, as depicted by **18**, would give the diradical **19**. Hydrogen transfer *via* an ideal six-membered transition state would give the new diradical **20**. Intramolecular radical combination would produce the observed product, **12**.

The addition of benzyne to **7** from inside the sterically hindered flap formed by the fused rings of the bicyclo[1.1.0]butane portion of **7** demonstrated the overwhelming preference for backside attack on the

(25) The hydrogenation product was identical in all respects with an authentic sample of *endo*-2-phenylnorbornane kindly provided by Professor H. C. Brown; K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2693 (1968).
(26) For a discussion of molecular orbital symmetry considerations in relation to 2 + 2 + 2 concerted reactions see R. Hoffmann and R. B. Woodward, *ibid.*, 87, 2046 (1965).

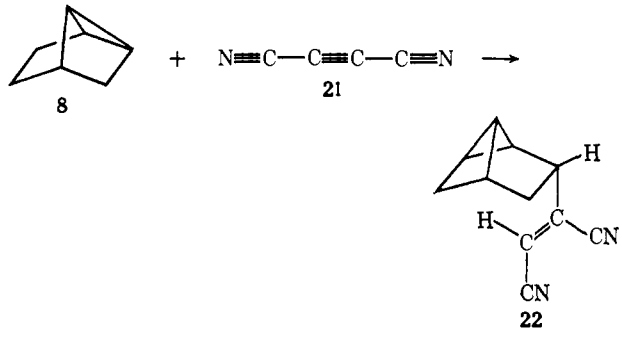
Chart II



bent σ bond of the tricyclic. The failure of the trimethylene bridge to stop the addition indicated that the approach of the bent bondophile could be end-on and thus that a symmetrical attack as shown in **5** was not a prerequisite for the reaction.

Having established the occurrence of an end-on approach of carbon–carbon multiple bonds to bent σ bonds, we desired to study the effect of the steric environment of the two ends of the strained bond on the initial point of attack. As noted above, **8** can be viewed as a derivative of bicyclo[2.1.0]pentane in which the two ends of the reactive bond are located in different steric environments. Benzyne, being a relatively poor bent bondophile, does not add to either bicyclo[2.1.0]-pentane or to **8** under conditions where bicyclo[1.1.0]-butane and its derivatives add benzyne readily. Thus the reaction of **8** with dicyanoacetylene was chosen for the investigation of the steric environment factor.

When **8** was treated with dicyanoacetylene (**21**) in a 1:1 ratio for **14** hr at 70° a crystalline adduct was obtained in 46% yield. Mass spectrometry showed a parent peak at *m/e* 170 which established the 1:1 nature of the adduct. The ultraviolet spectrum of the product was consistent with the presence of a monosubstituted



maleonitrile,[16] having $\lambda_{max}^{CH_3OH}$ 222 mμ (ϵ 8250). The infrared spectrum showed a nitrile absorption at 4.43 μ and a double bond stretching absorption at 6.23 μ. The near-infrared spectrum of the adduct formed from dicyanoacetylene and **8** had a maximum at 1.658 μ similar to that observed at 1.657 μ for **12**. The nmr spectrum of the product had a single olefinic proton which appeared as a doublet at τ 3.75 (J_{AB} = 2.5 cps) coupled to the single allylic proton at τ 6.25. The remainder of the upfield portion of the spectrum consisted of multiplets at τ 7.00 (1 H) and 7.40 (1 H), and a broad envelope of multiplets at τ 8.00–8.60 (6 H). The overall spectral data were most consistent with the adduct having structure **22**.

From a mechanistic viewpoint two products were reasonable. As shown in Chart III the attacking bent bondophile could approach from either the more hindered a side or from the less hindered b side of **8**. Attack following path a could produce the diradical **23** as the first intermediate. Hydrogen transfer would give a new diradical **24** which could intramolecularly cyclize to give the nortricyclane derivative **25**.

Initial addition of **21** to the less hindered b end of the bent bond of **8** would follow path b to give the diradical **26**. In principle either H_A, H_B, or H_C could be transferred to the vinylic radical center. However, it has been well established that intramolecular hydrogen transfer to radical centers prefers to occur *via* a six-membered transition state.[27] Since the transfer of H_C requires a five-membered transition state and the transfer of H_B requires a seven-membered transition state, the transfer of H_A, which can be accommodated by a six-membered transition state, should be the one which occurs. This would produce the diradical **27**, which would give **22** by intramolecular radical recombination. The unlikely transfer of either H_C or H_B would have eventually produced either **28** or **29**, respectively, by a similar set of reactions. Thus, attack at b should produce a derivative of tricyclo-[4.1.0.$0^{3,7}$]heptane (presumably **22**)[28] while attack at a can only give a derivative of tricyclo[2.2.1.$0^{2,6}$]heptane.[29]

Spectroscopic evidence was much more consistent with the adduct having structure **22** than with the structure being **25**. In addition it was possible to completely eliminate **25** by chemical degradation. As shown in Chart IV, the oxidation of **22** with osmium tetroxide in pyridine followed by treatment with hydrogen sulfide in tetrahydrofuran gave the keto acid **30**, which, without purification, was further oxidized with hydrogen peroxide to give **31**. If the structure of the adduct had been **25** rather than **22** the degradation product at this point would have been the known nortricyclanecarboxylic acid **32**. However, our degradation product was shown spectroscopically to be completely different from an authentic sample of **32**.[30] Moreover, the methyl ester **33** was shown to be non-identical with **34**. Final confirmation that the adduct possessed the tricyclo[4.1.0.$0^{3,7}$]heptyl skeleton was provided by the catalytic hydrogenation of **33** to give **35** which was identical in all respects with an authentic sample[31] of *endo*-2-carbomethoxybicyclo[2.2.1]heptane (**35**). Thus, it was demonstrated that the attacking bent bondophile was quite sensitive to the difference in the steric environment of the two ends of the bent σ bonds.

In summary we have shown that additions of carbon–carbon multiple bonds to bent carbon–carbon single

(27) R. S. Davidson, *Quart. Rev.* (London), **21**, 249 (1967).
(28) It should be noted that attack at C_b will give the tricyclo-[4.1.0.$0^{3,7}$]heptyl skeleton regardless of whether H_A, H_B, or H_C is transferred.
(29) A concerted 2 + 2 + 2 reaction would also be expected to yield **22** *via* attack at C_b and **25** *via* attack at C_a.
(30) K. Alder, R. Hartmann, and W. Roth, *Ber.*, **93**, 2271 (1960).
(31) O. Diels and K. Alder, *Ann.*, **98**, 460 (1928).

Chart III

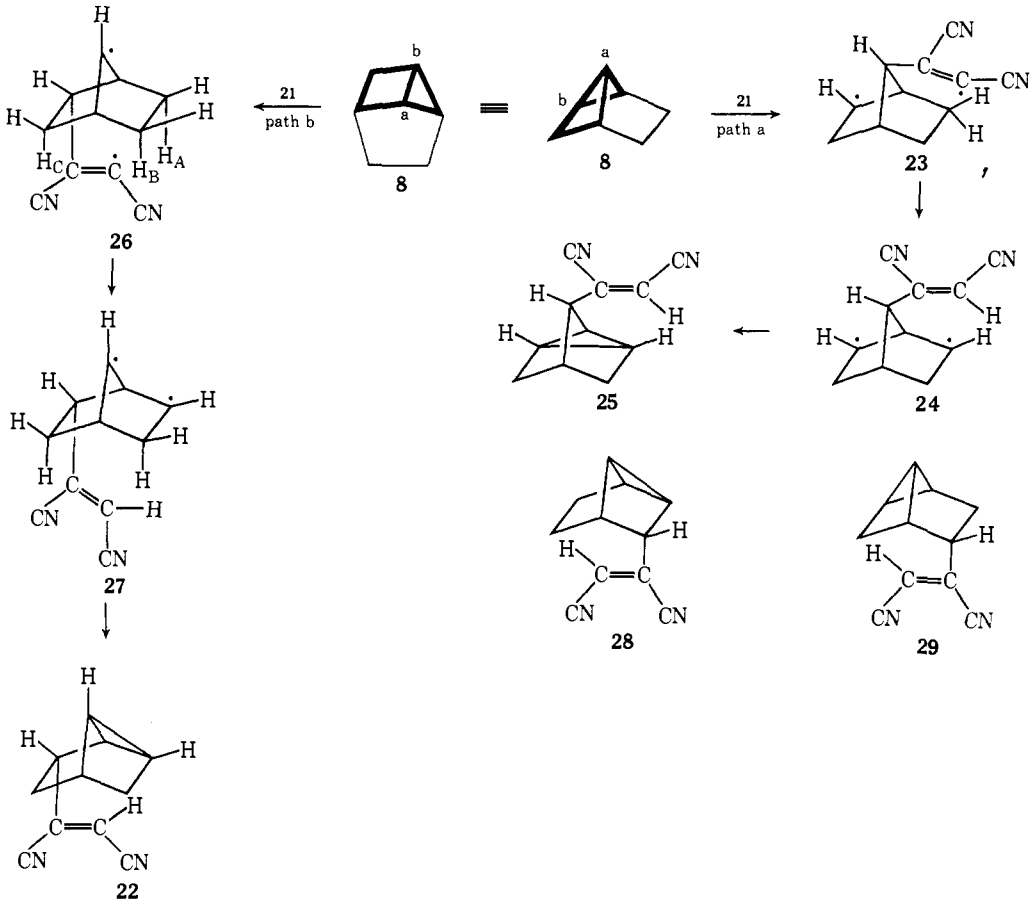
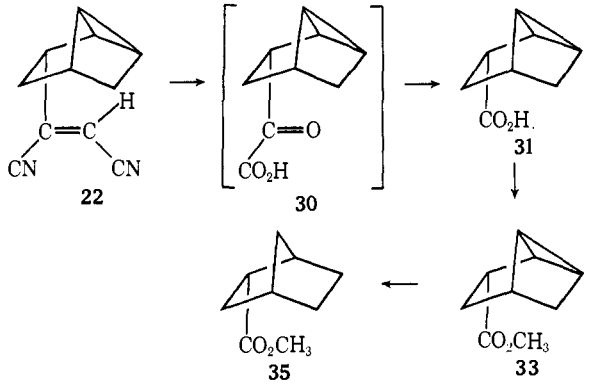


Chart IV



bonds occur from the backside of the bent σ bond even when the inside of the flap is protected by a small methylene bridge. Thus an end-on approach to the

inside of the flap formed by the fused rings of the small bicyclic moiety is required. This end-on approach to the backside of the bent σ bond is relatively sensitive to the steric environment of the two ends of the bent bond and selectively occurs at the less hindered end.

Experimental Section[32]

Tricyclo[4.1.0.0^{3,7}]heptane (7). The tricyclic hydrocarbon 7 was prepared by a modification of the procedure of Moore, Ward, and Merritt.[14] A solution of 120 g of 7,7-dibromonorcarane[33] in 200 ml of anhydrous ether was placed under a nitrogen atmosphere and cooled to 0° in a salt–ice–water bath. Methyllithium (330 ml of a 5.18% ether solution, Foote Chemical Co.) was added *via* syringe at approximately 200 ml per hr and the temperature was maintained between 0 and 5°, with vigorous mechanical stirring. Stirring was continued for 0.5 hr after addition was complete. An additional 114 g of 7,7-dibromonorcarane was similarly treated. The resulting reaction solutions were poured into 1 l. of an ice–water mixture. The layers were separated and the water portion was extracted with ether. The combined ether solutions were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the ether was removed by distillation through a packed column. The residue was distilled at 80–130°, at atmospheric pressure. Careful redistillation of this crude distillate on a spinning-band column at atmospheric pressure afforded 17.0 g (20%) of 7, bp 111–112°. Vpc analysis on a 15% TEG column at 50° indicated a 3–4% impurity which was presumably the tricyclo[4.1.0.0^{3,7}]heptane isomer.

Addition of Benzyne to 7. The benzyne precursor, benzenediazonium-2-carboxylate, was prepared from anthranilic acid, isoamyl nitrite, and a catalytic amount of trichloroacetic acid in dry THF at room temperature.[18] The salt was isolated by decanting off the solvent and washing with THF followed by methylene chloride. A slurry of the diazonium salt (from 9 g of anthranilic acid) in 30 ml of methylene chloride was refluxed (40°) with 2.00 g (2.12 mmol) of 7 for 4 hr. Gas evolution ceased and the mixture became dark brown. The methylene chloride was removed by distillation through a packed column. The residue was extracted with ether and washed with a saturated sodium carbonate solution to remove

(32) Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 infracord as neat liquids, solutions, or powdered solids in potassium bromide disks. Near-infrared spectra were obtained on a Cary Model 14 recording spectrometer from 1 *M* solutions in A. R. carbon tetrachloride. Ultraviolet spectra were recorded on the same instrument. Nuclear magnetic resonance spectra were obtained on Varian Associates A-60, A-60-A, and HA-100 spectrometers and reported in τ units relative to tetramethylsilane (τ 10.00).

(33) W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 76, 6162 (1954).

benzoic acid. Removal of the ether followed by distillation of the residue gave a fraction (0.165 g) boiling at 110–115° (1 atm) which was shown by vpc and infrared data to consist of chlorobenzene. Continued distillation gave 2.7 g of a second fraction, bp 87–91° (1.1 mm), which vpc analysis on a 5% SE-30 column showed to contain approximately 4% impurity of comparable molecular weight plus some higher molecular weight impurities. Chromatography on silica gel gave 2.2 g (61%) of **12**, bp 77–78° (0.55 mm), containing approximately 3% impurity. Preparative vpc with 20% SE-30 on 60–80 Chrom W column (10 ft) afforded an analytical sample of 2-phenyltricyclo[4.1.0.0^{3,7}]heptane (**12**).

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.83; H, 8.27.

When the reaction was completed on the same scale with THF rather than methylene chloride as the solvent, no chlorobenzene was formed and 1.4 g (39%) of **12** was obtained after chromatography.

The infrared spectrum showed bands at 13.80 and 14.40 μ and a pattern of absorptions in the 5.00–5.70-μ region characteristic of a monosubstituted aromatic compound. The ultraviolet spectrum showed a nonconjugated benzene ring. The nmr spectrum (neat) showed a singlet at τ 2.94 (5 H), a quartet at τ 6.38 (1 H), a complex doublet at τ 7.24 (1 H), a multiplet at τ 7.75 (1 H), and a broad multiplet at τ 8.1–9.0 (6 H). The near-infrared spectrum showed maxima at 1.657 (ϵ 0.810) and 1.673 μ. The parent peak in the mass spectrum appeared at *m/e* 170. An intense peak at *m/e* 91 was also present. The reaction product reacted rapidly with bromine in carbon tetrachloride and slowly decolorized aqueous potassium permanganate but was unreactive to ozone in methanol at room temperature and osmium tetroxide in ether.

Hydrogenation of 2-Phenyltricyclo[4.1.0.0^{3,7}]heptane (12). A solution of 170 mg (1 mmol) of **12** in 10 ml of ethanol over 50 mg of prereduced 5% palladium on carbon rapidly absorbed 1.0 equiv of hydrogen. Filtration of the catalyst followed by solvent removal yielded 170 mg (99%) of **17**. Vapor phase chromatography on a 5% SE-30 column revealed only one product. The near-infrared spectrum showed no cyclopropyl hydrogens. The nmr spectrum had a singlet at τ 2.86 (5 H), a broad five-peak multiplet at τ 6.60–7.00 (1 H), and multiplets at τ 7.5–7.8 (2 H), τ 7.95–8.30 (2 H), and τ 8.40–8.80 (6 H). The nmr and infrared spectra were identical with those of an authentic sample of **17** kindly furnished by Professor H. C. Brown. (The sample supplied by Professor Brown contained 13% 2-phenylnortricyclane and was purified by preparative chromatography on a 10 ft 25% XF-1150 on Chrom W column at 135°.)

1,7-Dideuteriotricyclo[4.1.0.0^{2,7}]heptane (7-d_2). The preparation of this compound was similar to that of the monodeuterated substance prepared by Closs.[24] Tricyclo[4.1.0.0^{2,7}]heptane (3.0 g) was added to 38 ml of a solution of *n*-butyllithium[34] freshly prepared from 4.3 g of lithium and 34.25 g of *n*-butyl bromide in 150 ml of anhydrous ether. This reaction mixture was allowed to stand for 6 hr and then quenched with 1.28 g of deuterium oxide. The lithium deuterioxide was removed by filtration and most of the ether was removed through a packed column. The procedure was repeated three additional times with the remaining hydrocarbon. Subsequent distillation gave 0.80 g of **7** which mass spectral data indicated was greater than 90% dideuterated.

Reaction of 1,7-Dideuteriotricyclo[4.1.0.0^{2,7}]heptane with Benzyne. The procedure was the same as for the undeuterated compound. From 800 mg of 7-d_2, 387 mg (27%) of dideuterated adduct was obtained after chromatography on silica gel. The nmr spectrum (CCl_4) showed a singlet at τ 6.84 (5 H), a broad singlet at τ 7.20 (1 H), and a multiplet at τ 8.15–9.0 (6 H). The peaks at τ 6.38 and 7.75 in the spectrum of the undeuterated adduct had disappeared. The mass spectrum showed a parent peak at *m/e* 172 and the major fragmentation peak at *m/e* 92 ($C_7H_6D^+$), compared with an intense peak at *m/e* 91 for the undeuterated adduct.

Tricyclo[4.1.0.0^{3,7}]heptane[35] (8). The tricyclic hydrocarbon **8** was prepared according to a slight modification of the procedure of Brown and Bell.[15] *anti*-7-Hydroxynorbornene (35.6 g), prepared according to the procedure of Story,[36] was added to 70.0 g of *p*-toluenesulfonyl chloride in 200 ml of pyridine and the reaction mixture was allowed to stand at 0° for 12 hr. The mixture was poured into 1.0 l. of ice water containing 200 ml of concentrated hydrochloric acid and extracted with chloroform. The extracts were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the drying agent and solvent gave a yellow oil (80%) which crystallized upon cooling and trituration with Skelly B. Due to its tendency to decompose, the *anti*-7-tosyloxynorbornene was not recrystallized. A solution of the tosylate in 50 ml of THF was added over 15 min to 20.0 g of lithium aluminum hydride in 600 ml of THF while maintaining the reaction mixture at room temperature. After the mixture was stirred for an additional 2 hr, 80 ml of water was added dropwise and stirring continued for 0.5 hr. Filtration was followed by removal of the THF by distillation through a packed column. The residue was distilled through a 6-in. Vigreux column at atmospheric pressure with collection of the distillate at 90–110°. Redistillation at 94–103° gave 8.0 g (26% from *anti*-7-hydroxynorbornene) of a mixture of **8** and norbornene in the approximate ratio of 3:2 by vpc analysis (15% TEG) as previously reported.[15] Elution of this mixture with purified pentane from 100 g of a 10% saturated silver nitrate–alumina column gave 3.07 g of pure **8**. The nmr spectrum (neat) showed a broad envelope of overlapping multiplets from τ 7.40 to 9.35.

Dicyanoacetylene (21). In a procedure similar to that of Blomquist,[37] dehydration of 11.0 g of acetylenedicarboxamide with 60 g of phosphorus pentoxide in 80 g of fine sand at 180–210° (2 mm) for 0.5 hr yielded 0.8–1.4 g (11–19%) of **21**. Substitution of dry nitrogen for carbon dioxide in this procedure gave only slightly reduced yields.

Addition of Dicyanoacetylene (21) to 8. A mixture of 400 mg (5.26 mmol) of **21** and 500 mg (5.31 mmol) of **8** was sealed under nitrogen in a glass ampoule and heated for 14 hr at 70°. Extraction of the crude reaction mixture with 20 ml of ether followed by removal of the solvent gave 410 mg (46%) of **22** as a light brown oil which slowly crystallized upon cooling and trituration with Skelly B. Under reaction conditions of 80° for 10 hr and 60° for 20 hr, the yield was approximately 25%. Thin layer chromatography on silica gel with benzene and ether–Skelly B showed only one component plus some polymeric material. The product was dissolved in four successive 25-ml portions of Skelly B at room temperature. Slow cooling of the combined solutions in a Dry Ice bath gave **22** as small white needles, mp 58–59°.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.59; H, 5.77; N, 16.27.

Homogeneity of the crystalline material was shown by vpc analysis on a FS-1265 column at 200°. The residue in the mother liquor after two additional crops of crystals were removed indicated that the crude reaction product was contaminated with approximately 5% impurity. The infrared spectrum had a nitrile absorption at 4.43 μ and a weak double bond absorption at 6.23 μ. The near-infrared spectrum showed maxima at 1.658 μ (ϵ 0.909) and 1.676 μ. The ultraviolet spectrum (methanol) had λ_{max} 222 mμ (ϵ 8250). The nmr showed a single olefinic proton at τ 3.75 (doublet) which was coupled with a single allylic proton at τ 6.25 (J_{AB} = 2.5 cps) as determined *via* spin decoupling. The remainder of the spectrum consisted of multiplets at τ 7.00 (1 H), τ 7.40 (1 H), and τ 8.00–8.60 (6 H). The parent peak in the mass spectrum appeared at *m/e* 170.

Conversion of Tricyclo[4.1.0.0^{3,7}]heptyl-5-maleonitrile (22) to 5-Carbomethoxytricyclo[4.1.0.0^{3,7}]heptane (32). After standing at room temperature for 12 hr, a solution of 200 mg (1.07 mmol) of **22** and 300 mg (1.08 mmol) of osmium tetroxide in 15 ml of ether and 4 ml of pyridine produced a light brown crystalline precipitate.[38] The precipitate was washed with three 5-ml portions of ether and slurried with 6 ml of THF. A slow stream of hydrogen sulfide[39] was passed through the slurry for 0.5 hr and the mixture was allowed to stand for an additional 0.5 hr. The precipitated osmium dioxide was removed by filtration. The residue remaining after solvent removal was dissolved in 4 ml of 5% sodium hydroxide solution, followed by addition of 0.5 ml of 30% hydrogen peroxide with cooling. After standing at room temperature for 2 hr the solution was washed with ether. The aqueous solution was made slightly acidic (pH 6) with 10% hydrochloric acid and extracted with ether. Removal of the ether after drying over anhydrous magnesium sulfate gave 48 mg of a clear oil. The infrared spectrum showed the presence of a carboxylic acid function. Analysis

(34) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 352 (1951).

(35) Although the literature[14,15] name for **8** has been used throughout this paper, the more acceptable name would be tricyclo[3.2.0.0^{2,7}]heptane.

(36) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(37) A. T. Blomquist and E. C. Winslow, *ibid.*, 10, 149 (1945).

(38) R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 99 (1942).

(39) R. Hirschmann, G. A. Bailey, R. Walker, and J. M. Chemerda, *J. Amer. Chem. Soc.*, **81**, 2822 (1959).

on a 3% FFAP on 46–60 Chrom W vpc column at 190° indicated two products. The minor component was assumed to be the epimeric acid and represented 10–30% of the mixture depending on reaction conditions. The acids were not separated but were converted quantitatively to their methyl esters with diazomethane. Separation of the esters on a 25% XF-1150 preparative column gave 14 mg of the major component and 3 mg of the minor one. The mass spectrum of the major ester, 5-carbomethoxytricyclo[4.1.0.0^{3,7}]heptane (**32**), showed a parent peak at *m/e* 152.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.78; H, 7.97.

The infrared spectrum (neat) of this ester was not superimposable on that of an authentic sample of 3-carbomethoxynortricyclanecarboxylic acid.[30] An nmr spectrum was obtained on a small amount of ester formed from a repetition of the degradation sequence. Although this sample contained approximately 10% impurity, the spectrum was similar to that of the original adduct and not to that of the corresponding nortricyclanecarboxylic ester.

An accurate mass measurement (found: *m/e* 152.0845. calcd: *m/e* 152.0834) of the minor ester component showed it to be isomeric with **32**.

Hydrogenation of 5-Carbomethoxytricyclo[4.1.0.0^{3,7}]heptane (32) to *endo*-2-Carbomethoxynorbornane (35). Into a 5-ml side-arm flask fitted with rubber septums was placed 20 mg of **32**, 4 mg of 5% Pd–C, and 3 ml of ether. The flask was flushed with hydrogen and a positive hydrogen pressure was introduced *via* a syringe. Vpc analysis on a 2% XF-1150 column indicated hydrogenation was 80% complete after overnight stirring. The catalyst was removed by centrifugation and 10 mg of fresh catalyst was added. Completion of hydrogenation in 20 min gave 12 mg of product which was purified by means of a 3% PDEAS (1/4 in. × 8 ft) vpc column at 86°. The nmr and infrared spectra were identical with those of an authentic sample of **35**. The nmr spectrum was obtained on an A-60-A spectrometer coupled with a transient averaging computer (27 scans, 250 sec each).

***endo*-2-Carbomethoxybicyclo[2.2.1]heptane (35).** A known sample of 1.0 g (7.25 mmol) of *endo*-5-norbornene-2-carboxylic acid was quantitatively hydrogenated over 80 mg of 5% Pd–C in 20 ml of ethanol in less than 1 hr. The saturated acid was converted to its methyl ester,[31] with diazomethane in ether. The nmr spectrum had a singlet at τ 6.63 (3H), a broad multiplet at τ 7.30–8.47 (3 H), and a multiplet at τ 8.47–9.47 (8 H).

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Direct Fluorination of Ureas[1]

Vytautas Grakauskas and Kurt Baum

Contribution of the Environmental Systems Division, Aerojet-General Corporation, Azusa, California. *Received October 1, 1969*

Abstract: Fluorourea and N,N-difluorourea were prepared by the direct fluorination of aqueous solutions or acetonitrile suspensions of urea. Fluorourea decomposed in aqueous solution to give azodicarbondiamide, and in the presence of urea, biurea. Fluorourea reacted with sulfuric acid to give fluorammonium ion, ammonium sulfite, or hydrazine sulfate, depending on reaction conditions. Properties of N,N-difluorourea are described. The fluorination of alkylureas gave difluoraminoalkanes and N-alkyl-N′,N′-difluoroureas, showing that the second fluorination step takes place at the same nitrogen as the first, whether a hydrogen or an acyl group is displaced. The fluorination of cyclic N,N′-disubstituted ureas gave ω-(difluoramino) isocyanates and carbamyl fluorides.

The fluorination of solid urea was reported by Glemser and Lüdemann[2] to give biurea and HF, along with some NH_3, COF_2, CO_2, and biuret. Although no NF compounds were identified, fluorourea was postulated to be an intermediate. Subsequently, Lawton, *et al.*,[3,4] identified N,N-difluorourea as one of the products of fluorination under similar conditions, as well as CF_4, $(CF_3)_2NF$, $(CF_3)_3N$, HNF_2, and HCN. Less than 1 mole of fluorine per mole of urea was used.

The fluorination of aqueous solutions of urea was found in the present work[5] to be a more readily controllable reaction to produce N,N-difluorourea. This solution fluorination technique has also been applied to carbamates,[6,7] amides,[8] and nitronate salts.[9] The moderating effect of the solvent allowed the use of 2 moles of fluorine, and a 74% yield of N,N-difluorourea was isolated by ether extraction. N,N-Difluorourea was also prepared by the fluorination of a suspension of urea in acetonitrile.

N,N-Difluorourea must be handled with caution, as it is a sensitive explosive and is toxic, but it is not changed on prolonged storage at room temperature. A sample was recovered almost quantitatively after 5 hr in toluene at 110°. The compound is a white solid, mp 41–41.5°, which was isolated in two crystalline forms, platelets by sublimation and needles by crystallization from halogenated solvents. The platelet form is hygroscopic whereas the needle form is not affected by atmospheric moisture. The amino group of N,N-difluorourea is unreactive, and further fluorination did not yield more highly fluorinated ureas.[10] No reaction took place in 5 hr between difluorourea and bromine in carbon tetrachloride at 60°.

(1) This work was supported by the Office of Naval Research and the Advanced Research Projects Agency.

(2) O. Glemser and H. Lüdemann, *Z. Anorg. Allgem. Chem.*, **286**, 168 (1956).

(3) E. A. Lawton, E. F. C. Cain, D. F. Sheehan, and M. Warner, *J. Inorg. Nucl. Chem.*, **17**, 188 (1961).

(4) E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **85**, 3595 (1963).

(5) Preliminary communication: V. Grakauskas, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 23M.

(6) V. Grakauskas and K. Baum, *J. Am. Chem. Soc.*, **91**, 1679 (1969).

(7) V. Grakauskas and K. Baum, *J. Org. Chem.*, **34**, 2840 (1969).

(8) V. Grakauskas and K. Baum, *ibid.*, in press.

(9) V. Grakauskas and K. Baum, *ibid.*, **33**, 3080 (1968).

(10) Tetrafluorourea has been prepared from difluorocarbamyl fluoride and alkali fluorides: G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, **6**, 1711 (1967).