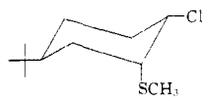
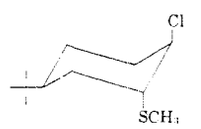
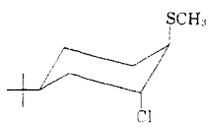
TABLE II

RATES OF SOLVOLYSIS OF CHLORO SULFIDES

Compd	Infrared absorptions, μ	Isomeric purity, %	Found, %[a] C	Found, %[a] H	Temp, °C	k^t, sec^{-1} $\times 10^6$ [b]
	11.48, 14.52	100	59.96	9.80	100	0.54
	12.90, 14.27	~70	60.04[c]	10.12[c]	100	6
	13.63				25.2	48
						Probably same as VII
	14.72	>87	59.99	9.54	24.9	730

[a] *Anal.* Calcd for $C_{11}H_{21}ClS$: C, 59.83; H, 9.59. [b] Ethanol–water (80:20). [c] Recrystallization residue.

was obtained. *trans*-3-Methylmercapto-*trans*-4-chloro-*t*-butylcyclohexane (II) was the predominant product in all fractions as indicated by infrared analysis (characteristic absorption at 14.52 μ). The absorption at 14.72 μ due to VII (*trans*-3-chloro-*cis*-4-methylmercapto-*t*-butylcyclohexane) was prominent in the spectra of the first three fractions, decreasing in intensity in going from fraction 1 to 3; the 14.72-μ band was not present before distillation. Fractions 4 and 5 appeared to be relatively pure adduct II, the spectrum of fraction 5 showing a small absorption band at 14.3 μ attributed to adduct III.

Recrystallization from pentane at −70° separated pure II, mp 35–36°, concentrating the other isomers in the mother liquors. The lower-boiling fractions were richest in VII, the higher-boiling fractions in III. Maximum purities, compositions, etc. are listed in Table II.

Recrystallization of a crude reaction mixture prior to distillation yielded a concentrate of III (12.90 and 14.27 μ) and IV (13.63 μ), uncontaminated by VII (14.72 μ). Extended vacuum distillation or heating in a sealed ampoule (130–140°, 4 hr) resulted in nearly complete conversion of III to VII as evidenced by changes in the infrared spectrum and an increase in the rate of solvolysis of the rapid-solvolyzing component.

Pure II was oxidized with 30% hydrogen peroxide in glacial acetic acid to the sulfone, mp 141–142.5°.

Anal. Calcd for $C_{11}H_{21}ClO_2S$: C, 52.26; H, 8.37. Found: C, 52.19; H, 8.36.

7-Azabenzonorbornadiene[1]

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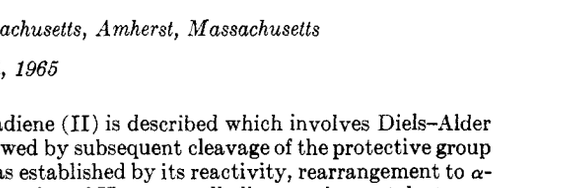
A practical method for the synthesis of 7-azabenzonorbornadiene (II) is described which involves Diels–Alder addition of benzyne to *t*-butyl pyrrole-1-carboxylate (IX) followed by subsequent cleavage of the protective group by hydrogen chloride in nitromethane. The structure of II was established by its reactivity, rearrangement to α-naphthylamine, and spectral examination. Catalytic hydrogenation of II over a palladium–carbon catalyst gave the dihydro derivative XII. Both II and XII yielded N-nitroso derivatives, although that obtained from II was unusual in undergoing facile decomposition to naphthalene.

Because of their unique structural features 7-substituted 7-azanorbornadienes such as the 7-halo, 7-hydroxy, and 7-amino derivatives are of considerable theoretical interest.[2] Since nitrogen-unsubstituted 7-azanorbornadienes could probably be converted to such compounds by means of ordinary techniques, we have begun an investigation of the synthesis of 7-azanorbornadiene (I) and its mono- (II) and dibenzo



I II III

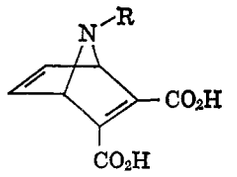
(III) derivatives. The present paper describes a practical route to the middle member (II) of the series.

The first authentic derivative of the 7-azanorbornadiene system was reported by Mandell and Blanchard,[3] who showed that the 7-benzyl-2,3-dicarboxylic acid

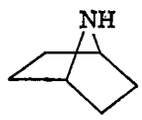
(1) Abstracted from a portion of the thesis submitted by D. E. Barr in partial fulfillment of the requirements for the Ph.D. degree, 1965. Supported in part by the National Science Foundation under Grants NSF G-19506 and GP-4283.

(2) For a review of the interesting effects observable in the corresponding carbon compounds, see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 192–205.

(3) L. Mandell and W. A. Blanchard, *J. Am. Chem. Soc.*, **79**, 6198 (1957).



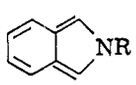
IV



V

(IV, R = $C_6H_5CH_2$) could be obtained in low yield by reaction of N-benzylpyrrole with acetylenedicarboxylic acid. Subsequently, the same method was applied to the synthesis of the N-α-menaphthyl derivative (IV, R = α-$C_{10}H_7CH_2$).[4] The only other example of a compound incorporating this ring system was described by Acheson and Vernon,[5] who isolated the carbomethoxy derivative (IV, R = $COOCH_3$) in 6% yield by a similar reaction. In general, most attempts to carry out Diels-Alder reactions between simple pyrroles and acetylene derivatives have led to α substitution or normal Diels-Alder addition followed by subsequent retrogression,[6] or further transformations[7] of the initial adduct. Even the saturated analogs of I have been difficultly available and therefore virtually unknown. von Braun and Schwarz[8] reported the formation of 7-azanorbornane (V) in low yield by reaction of 4-bromocyclohexylamine with potassium hydroxide. The corresponding N-methyl derivative has been obtained in 11% yield by means of the Hofmann–Löffler–Freytag reaction.[9] More recently[10] 1,3-dipolar cycloadditions involving azlactones and various dipolarophiles have given a number of highly substituted derivatives of V.

A few N-alkyl- and N-aryl-7-azabenzonorbornenes have been prepared by reaction of N-substituted isoindoles (VI, R = alkyl, aryl) with dienophiles such as maleic anhydride.[11] Recently this method has

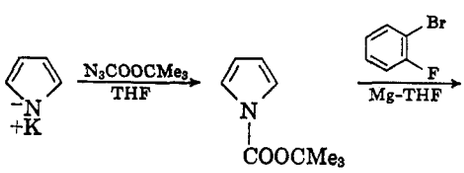


VI

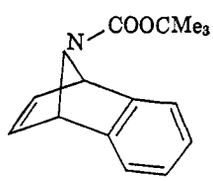
VII

been applied to isoindole itself (VI, R = H), which has not yet been isolated although it can be generated in solution and trapped in the expected manner by the Diels–Alder reaction.[12] Derivatives of III have been obtained similarly.[13] Reaction of N-methyl- and N-benzylpyrrole (VII, R = CH_3 and $C_6H_5CH_2$) with benzyne gave in low yields the expected N-methyl and N-benzyl derivatives of II, which, however, were isolated only in the form of the methiodide and picrate, respectively.[14,15] By utilizing pyrrylmagnesium iodide in place of substituted pyrroles, Wittig and Reichel[15] succeeded in obtaining the hydrobromide of 7-azabenzonorbornadiene (II·HBr) in 6% yield. Conversion of the hydrobromide to the free base was also reported, but II was probably obtained only in trace amounts by this method since it was not completely characterized. Subsequent to the work of Wittig and Reichel, Wolthuis and co-workers[16] studied the addition of benzyne to a number of 1,2,5-trisubstituted pyrroles and were unable to isolate the primary Diels–Alder adducts but instead obtained only the rearranged β-naphthylamines. Substituents in the 2- and 5-positions of the starting pyrrole may facilitate this rearrangement.

In the present study we were able to develop a practical route to II and obtain this interesting compound in sufficient quantity for complete characterization. No difficulty was encountered in handling the free base, although ring opening to α-naphthylamine was noted under a variety of acidic conditions. The method employed in the synthesis of II was essentially that of Wittig except that an easily cleaved protective group was used to cover the nitrogen atom until after the Diels–Alder reaction. Reaction of the potassium salt of pyrrole with *t*-butyl azidoformate[17] gave in 61–75% yield *t*-butyl pyrrole-1-carboxylate (IX), which in the presence of benzyne generated from *o*-bromofluorobenzene and magnesium in tetrahydrofuran gave the adduct X in 35–41% yield.



VIII IX



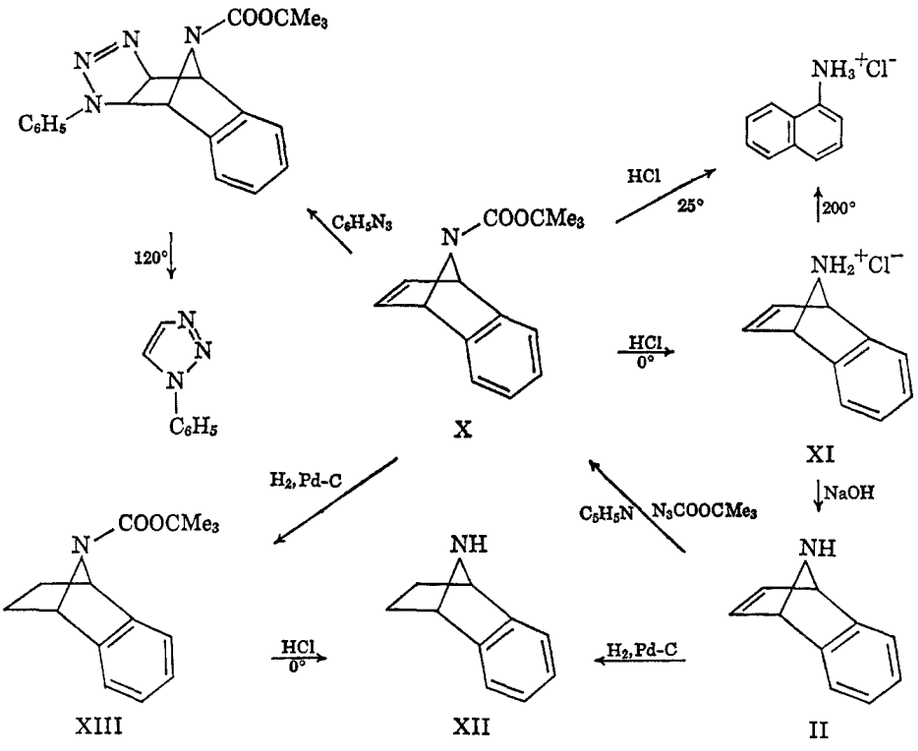
X

Attempts to cleave the carbo-*t*-butoxy group from the Diels–Alder adduct by passage of gaseous hydrogen chloride through a solution of X in nitromethane at room temperature gave mainly α-naphthylamine hydrochloride. (See Chart I.) However, if the cleavage was carried out at 0°, the bicyclic system remained intact and the expected hydrochloride XI was isolated easily in good yield. At its melting point (200°) XI underwent conversion to α-naphthylamine hydrochloride. The bicyclic nature of X and its subsequent transformation products was established by chemical and spectral methods. As expected for a system with a strained double bond, X reacts readily with phenyl azide[18] to give an adduct (Chart I) which on pyrolysis yields 1-phenyl-1,2,3-triazole.

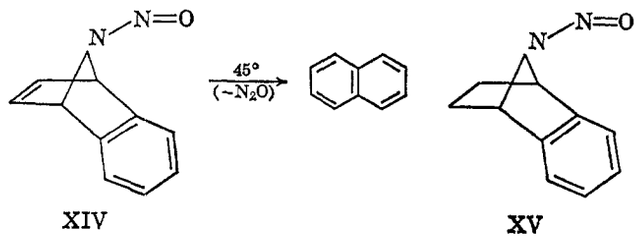
Evidence for the intact nature of the bicyclic system in II comes from both the ultraviolet spectrum [$\lambda_{max}^{C_2H_5OH}$,

(4) L. Mandell, J. U. Piper, and C. E. Pesterfield, *J. Org. Chem.*, **28**, 574 (1963).
(5) R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1008 (1963).
(6) R. M. Acheson and J. M. Vernon, *ibid.*, 457 (1961); N. W. Gabel, *J. Org. Chem.*, **27**, 301 (1962).
(7) R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1148 (1962); R. M. Acheson, A. R. Hands, and J. M. Vernon, *Proc. Chem. Soc.*, 164 (1961).
(8) J. von Braun and K. Schwarz, *Ann.*, **481**, 56 (1930).
(9) R. Lukes and M. Ferles, *Collection Czech. Chem. Commun.*, **20**, 1227 (1955).
(10) R. Huisgen, H. Gotthardt, and H. O. Bayer, *Tetrahedron Letters*, 481 (1964).
(11) G. Wittig, H. Tenhaeff, W. Schock, and G. Koenig, *Ann.*, **572**, 1 (1951); G. Wittig and H. Streib, *ibid.*, **584**, 1 (1953); G. Wittig and H. Ludwig, *ibid.*, **589**, 55 (1954); W. Theilacker and H. Kalenda, *ibid.*, **584**, 87 (1953); G. Wittig, G. Closs, and F. Mindermann, *ibid.*, **594**, 89 (1955).
(12) R. Kreher and J. Seubert, *Z. Naturforsch.*, **20b**, 75 (1965).
(13) G. Wittig, W. Stilz, and E. Knauss, *Angew. Chem.*, **70**, 166 (1958).
(14) G. Wittig and W. Behnisch, *Ber.*, **91**, 2358 (1958).
(15) G. Wittig and B. Reichel, *ibid.*, **96**, 2851 (1963).
(16) E. Wolthuis, D. VanderJagt, S. Mels, and A. DeBoer, *J. Org. Chem.*, **30**, 190 (1965).
(17) L. A. Carpino, B. A. Carpino, P. J. Crowley, C. A. Giza, and P. H. Terry, *Org. Syn.*, **44**, 15 (1964).
(18) Adduct formation with phenyl azide, characteristic of the strained double bonds in norbornene derivatives, has been reviewed by R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 565 (1963).

CHART I



mμ (log ε), 269 (3.15), 274.8 (3.18), and 282.2 (3.11)], clearly distinguishable from that of α-naphthylamine, and the nmr spectrum, which exhibits a singlet at δ 2.80 (1 H) due to the N–H proton, a multiplet centered at 6.75 (6 H) due to the combined aromatic and olefinic protons, and a triplet at 4.62 (2 H) arising from the bridgehead protons. As additional evidence for lack of skeletal change in the cleavage of X, amine II could be acylated with *t*-butyl azidoformate in pyridine solution to give back the original adduct (X).[19] The unsaturated amine (II) was easily reduced catalytically over palladium on carbon to the dihydro derivative XII. This change is readily followed in the nmr spectra, which show the disappearance of two protons from the aromatic–olefinic region and the appearance of four protons in the methylene area. These latter appear as two sets of complex multiplets centered at δ 1.19 (2 H) and 1.98 (2 H) arising from the *endo*- and *exo*-2,3-protons, respectively.[20] The free dihydroamine XII was also obtained by cleavage of the dihydrocarbo-*t*-butoxy derivative XIII. 7-Azabenzonorbornadiene and 7-azabenzonorbornene were characterized as their N-nitroso derivatives. The nitrosamine (XIV) derived from 7-azabenzonorbornadiene proved to be quite unstable. Slowly at room temperature and rapidly at 45° XIV underwent smooth decomposition to naphthalene and presumably nitrous oxide. On the other hand, the nitrosamine (XV) derived from the saturated analog XII was stable even up to 100°. Hydrogen chloride cleavage of the two nitroso compounds regenerated the starting amines, whereas catalytic reduction over palladium on carbon gave in both cases only the saturated free base XII.



XIV XV

Experimental Section[21]

***t*-Butyl Pyrrole-1-carboxylate (IX).**—A solution of 16.8 g of pyrrole in 100 ml of tetrahydrofuran was stirred under nitrogen at room temperature and 7.8 g of potassium was added in small pieces. The vigorously stirred mixture was warmed until all of the metal had dissolved (about 3 hr) and then cooled to 0° in an ice–salt bath, and a solution of 28.6 g of *t*-butyl azidoformate[17] in 50 ml of tetrahydrofuran was added over a period of 2–3 hr while keeping the temperature at 0°. After an additional 2 hr in the ice–salt bath, the mixture was warmed to room temperature, and 100 ml of ether and 100 ml of water were added. The organic layer was separated and the aqueous layer was extracted with two additional 50-ml portions of ether. The combined organic layers were washed twice with 50-ml portions of water and dried (magnesium sulfate), and the solvent was removed with water-bath heating with the aid of a water aspirator.

Two distillations through an 18-in. Vigreux column gave 20–25 g (61–75%) of the pyrrole: bp 91–92° (20 mm); nmr, δ^{CDCl_3} 1.50 [9 H, singlet, $C(CH_3)_3$], 6.18 (2 H, triplet, 3,4-H), and 7.22 (2 H, triplet, 2,5-H); $\lambda_{max}^{C_2H_5OH}$ 227 mμ (log ε 4.9).

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.58; H, 7.58; N, 8.50.

7-*t*-Butyloxycarbonyl-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (X).—A 500-ml flask fitted with a magnetic stirrer, condenser, dropping funnel, and nitrogen inlet tube was charged with 32 g of *t*-butyl pyrrole-1-carboxylate, 4.8 g of magnesium turnings, and 120 ml of tetrahydrofuran which had been freshly distilled from lithium aluminum hydride. The system was

(19) The method described for *t*-butyl hydrazodiformate was used. See L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957).

(20) Assignment of the *endo*- and *exo*-2,3-protons is based on the work of K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsugi, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(21) Melting points and boiling points are uncorrected. Elemental analyses are by A. Bernhardt, Mülheim (Ruhr), Germany. Unless otherwise indicated, nmr spectra were taken in deuteriochloroform on a Varian A-60 instrument using tetramethylsilane as internal indicator. Infrared and ultraviolet spectra were recorded on Beckmann IR-5 and Cary 14 spectrometers, respectively.

flushed with nitrogen for 15 min and heated to gentle reflux, and about 25% of a solution of 33.6 g of *o*-fluorobromobenzene[22] in 90 ml of tetrahydrofuran was added. After initiation of the reaction as evidenced by development of a yellow color accompanied by vigorous boiling, the remaining solution was added dropwise over a period of 30 min. The solution was refluxed for 90 min, cooled in an ice bath to 5°, and poured into a solution of 150 g of ammonium chloride and 5 ml of concentrated ammonium hydroxide in 500 ml of water. The aqueous layer was extracted with two 200-ml portions of tetrahydrofuran. The combined organic layers were dried over anhydrous potassium carbonate and the solvent was removed on a water bath with the aid of a water aspirator. The resulting dark oil was dissolved in 500 ml of petroleum ether (bp 60–80°) and the solution was filtered to remove a small amount of insoluble material. After removal of the solvent from a water bath with the aid of a water aspirator, the semisolid residue was triturated with 10 ml of cold (5°) petroleum ether (bp 30–60°). Filtration gave 24 g of light tan crystals, mp 65–70°. Sublimation in 10-g lots at 63° (0.05 mm) gave 16–19 g (35–41%) of the adduct as a white powder: mp 72–73°; nmr, δ^{CDCl_3} 1.32 [9 H, singlet, $C(CH_3)_3$], 5.42 (2 H, triplet, bridgehead protons), and 7.60 (6 H, multiplet, aromatic and olefinic protons).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.93. Found: C, 74.04; H, 7.00; N, 5.76.

2,3-Benzo-7-azabicyclo[2.2.1]hepta-2,5-diene Hydrochloride (II·HCl).—A stirred solution of 11 g of X in 200 ml of nitromethane was cooled to 0° in an ice–salt bath and hydrogen chloride gas was passed in very slowly for 20 min while keeping the temperature below 5°. Stirring was continued at 0–5° for 4 hr, and 200 ml of anhydrous ether was added to precipitate 7.7 g (97%) of the crude hydrochloride. This was pure enough for conversion to the free base (see below), although, since the material obtained in this way contains some α-naphthylamine hydrochloride, the analytical sample was prepared by passage of hydrogen chloride through a solution of 5 g of X in 100 ml of nitromethane for only 1 min followed by a 30-min period of stirring at 0°. Four sublimations at 120° (0.05 mm) gave the hydrochloride as a fine white powder, mp 198–200° dec.

Anal. Calcd for $C_{10}H_{12}ClN$: C, 66.11; H, 6.66; Cl, 19.51; N, 7.71. Found: C, 66.25; H, 6.83; Cl, 19.49; N, 7.61.

Pyrolysis of the hydrochloride by heating 0.3 g of the material in an oil bath at 200° for 2 hr gave 20 mg of α-naphthylamine hydrochloride (identified by infrared spectral comparison with an authentic sample) as a sublimate on the cooler parts of the tube. Wittig and Reichel[15] report a similar conversion for the hydrobromide.

2,3-Benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (II).—To a suspension of 15 g of crude 7-azabenzonorbornadiene hydrochloride in 100 ml of water there was added a solution of 10 g of sodium hydroxide in 130 ml of water. The mixture was extracted with four 200-ml portions of ether and the solvent was removed from the dried (magnesium sulfate) solution at room temperature with the aid of a water aspirator. Distillation of the residue over potassium hydroxide gave 6.1 g (51%) of the free base, bp 60° (0.4 mm).

Anal. Calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.75; H, 6.30; N, 9.94.

2,3-Benzo-7-azabicyclo[2.2.1]hept-2-ene (XII).—A solution of 6 g of II in 50 ml of 95% ethanol was hydrogenated in the presence of 0.5 g of palladium on carbon (10%) at room temperature and 40 psi. Filtration and evaporation gave 5 g (83%) of the saturated amine, mp 84–90°. Sublimation at 50° (0.05 mm) gave 4.3 g (72%) of white crystals: mp 96–98°; nmr, δ^{CDCl_3} 1.19 (2 H, multiplet, 2,3-*endo*-H), 1.98 (2 H, multiplet, 2,3-*exo*-H), 4.33 (2 H, multiplet, bridgehead), and 6.95 (4 H, multiplet, aromatic protons).

Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.56; H, 7.77; N, 9.51.

The **hydrochloride** was obtained by cleavage of XIII in the manner described for X. The yield of hydrochloride, mp 241–242° dec. was 85%. The compound sublimed at 180° (0.05 mm).

Anal. Calcd for $C_{10}H_{12}ClN$: C, 66.11; H, 6.66; Cl, 19.51; N, 7.71. Found: C, 66.25; H, 6.83; Cl, 19.49; N, 7.71.

Treatment of the hydrochloride with sodium hydroxide gave the free base, mp 96–98°, identified by infrared comparison with a sample prepared by hydrogenation of II.

***t*-Butyl 2,3-Benzo-7-azabicyclo[2.2.1]hept-2-ene-7-carboxylate (XIII).**—Catalytic hydrogenation of X by the method described for II gave the dihydro derivative in 86% yield as white crystals, mp 41–42°, purified by sublimation at 36° (0.05 mm): nmr, δ^{CDCl_3} 1.20 (2 H, multiplet, 2,3-*endo*-H), 2.05 (2 H, multiplet, 2,3-*exo*-H), 5.02 (2 H, multiplet, bridgehead), and 7.05 (4 H, multiplet, aromatic protons).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.67; H, 7.87; N, 5.82.

Phenyl Azide Adduct of *t*-Butyl 2,3-Benzo-7-azabicyclo[2.2.1]hepta-2,5-diene-7-carboxylate.—A solution of 1 g of X and 0.5 g of phenyl azide in 2 ml of dioxane was allowed to stand for 24 hr in a stoppered flask at room temperature in the absence of light. Filtration of the white crystals followed by washing with 3 ml of ethanol gave 1.3 g (88%) of the adduct, mp 133–134° dec. The analytical sample, mp 133–134° dec. was prepared by a single recrystallization from nitromethane–ethanol (1:1). Continued recrystallization of the material caused decomposition.

Anal. Calcd for $C_{21}H_{22}N_4O_2$: C, 69.59; H, 6.12; N, 15.46. Found: C, 69.62; H, 6.21; N, 15.32.

Pyrolysis of the phenyl azide adduct in a sublimation apparatus at 120° (0.05 mm) gave a sublimate consisting of 1-phenyl-1,2,3-triazole, mp 53–55°, lit.[23] mp 56°, identified by mixture melting point and infrared spectral comparison with an authentic sample. Wittig and Reichel[15] obtained the same compound on pyrolysis of the phenyl azide adduct of II.

7-Nitroso-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (XIV).[24]—To a mixture of 2.86 g of II and 6.5 g of sodium acetate in 60 ml of carbon tetrachloride which was kept at −15° by means of a Dry Ice–acetone bath there was added with stirring a solution of 1.64 g of nitrosyl chloride in 30 ml of cold carbon tetrachloride (−15°) at a rate to keep the temperature below −10°. Stirring was continued for 5 min at −10° and the mixture was washed quickly with 100 ml of 10% ice-cold potassium carbonate solution followed by 100 ml of ice water. The organic layer was dried over magnesium sulfate in an ice bath for 5 min and filtered, and the solvent was removed immediately with the aid of a vacuum pump at 10 mm. The residual brown crystals were sublimed at 35° (0.05 mm) to give 1.5 g (44%) of the nitroso compound as light yellow crystals, mp 49–51.5°.

Anal.[25] Calcd for $C_{10}H_8N_2O$: C, 69.75; H, 4.68. Found: C, 69.96; H, 4.66.

7-Nitroso-2,3-benzo-7-azabicyclo[2.2.1]hept-2-ene (XV).—Nitrosation following the procedure described above for the corresponding unsaturated analog gave the nitrosamine in 83% yield as light yellow crystals, mp 61–62°. The material was purified by sublimation at 45° (0.05 mm).

Anal. Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 68.93; H, 5.78; N, 16.26.

(22) *o*-Bromofluorobenzene, bp 66° (34 mm), was best prepared (61%) from *o*-fluoroaniline (Pierce Chemical Co., Rockford, Ill.) by the method described for *o*-bromochlorobenzene by J. L. Hartwell, "Organic Syntheses," Coll. Vol. III., John Wiley and Sons, Inc., New York, N. Y., 1965, p 185.

(23) A. Bertho, *Ber.*, **58**, 259 (1925).

(24) An outline of this procedure for the synthesis of labile nitrosamines was kindly supplied by Fr. C. J. Thoman, S.J.

(25) Because of the instability of XIV, the analytical sample, which possessed a strong odor of naphthalene on arrival at the microanalytical laboratory (5 days in transit), was evacuated at room temperature (2 mm) until this odor was no longer detectable just prior to analysis.