

Thin layer chromatography (silica–heptane) indicated a mixture of C_5Br_8 and $C_{10}Br_{10}$. The 42 g was dissolved in 400 ml of *n*-heptane (400 ml) and run through a silica (Davison 922 grade, 200–325 mesh) gel column. The first fraction gave 5.0 g of recovered C_5Br_8 , while the main fraction gave 27.4 g of $C_{10}Br_{10}$, mp 140.5–142°, an 85% yield based on recovered C_5Br_8 : ir (Nujol) 1626, 1579, 1550, 1287, 1183, 1148, 1099, 1000, and 692 cm^{-1} ; uv λ_{max}^{hexane} 333 nm (log ϵ 3.28); mass spectrum showed a molecular ion peak at m/e 910 (calcd for $C_{10}Br_{10}$, m/e 910). The mass spectrum itself is interesting in that it shows only ions resulting from the consecutive loss of bromine all the way from $C_{10}Br_{10}^+$ to C_{10}^+ ; each of these ions also had a doubly charged partner, which in most cases was the more intense.

Anal. Calcd for $C_{10}Br_{10}$: C, 13.07; Br, 86.93. Found: C, 13.20; Br, 86.80.

Isolation of $C_{10}Br_{10}$ (7) from the Preparation of Dodecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (6).—Hexabromocyclopentadiene (473 g, 0.875 mol) was placed in a 3-l., three-necked, round-bottomed flask equipped with a nitrogen inlet, a reflux condenser connected successively to a calcium chloride drying tube and a water scrubber, and a stirrer. Bromine (800 ml) was added and to the resulting solution was added 105 g of aluminum bromide. After refluxing for 45 hr water was added dropwise to destroy the aluminum bromide and the bromine was removed by steam distillation. The dark brown viscous oil remaining after removal of the bromine was treated with hot hexane leaving a dark brown solid. Recrystallization of the solid from THF–hexane gave about 120 g of pure $C_{10}Br_{12}$, mp 340–350° dec. The hexane washings proved to be a mixture of C_5Br_8 , another similar compound (later identified as $C_{10}Br_{10}$, 7) and an intractable tar. This last component was effectively removed by running the entire solution through a column of silica gel. After three recrystallizations of a sample of this material from 95:5 hexane–benzene a material was obtained having the physical appearance of C_5Br_8 but melting at 111–115°.² Mass spectrographic analysis of this material showed that it was a mixture of C_5Br_8 and a second component that was identified as $C_{10}Br_{10}$. The $C_{10}Br_{10}$ was obtained in pure form by removal of the C_5Br_8 by sublimation at 105° and 0.1 mm for 15 hr followed by recrystallization of the residue from 1:1 benzene–hexane. The material thus obtained was homogeneous to mass spectroscopy ($C_{10}Br_{10}$), was shown by ir to be free of C_5Br_8 and melted at 140–142°. Infrared and uv spectra were identical with those of 7 above.

Preparation of 6 from 7.—Compound 7 (5 g) was dissolved in bromine (20 ml) and 3 g of aluminum bromide was added. The mixture was stirred under reflux for 72 hr, cooled, water slowly added, and the bromine removed by steam distillation. Filtration of the residue gave a red solid that was added to 50 ml of benzene; after stirring for about 10 min the white solid (5.1 g) was collected by filtration. The solid thus obtained was shown by infrared analysis to be $C_{10}Br_{12}$ (6), yield 87%, mp 340–350° dec.

Registry No.—7, 25568-68-7.

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Novel "Meisenheimer" Complexes.

Alkyl-2,4,6-trinitrocyclohexadienate Anions

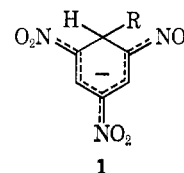
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1,3,5-Trinitrobenzene (TNB) reacts with a variety of anionic bases to yield brightly colored solutions of species known as "Meisenheimer" compounds (σ com-

plexes, 1, where R = $-OH$, $-OCH_3$, $-CH_2COCH_3$, $-CH_2NO_2$, $-CN$).²⁻⁵ Such structures have been postulated as intermediates in nucleophilic aromatic substitution reactions, and, in a few instances, stable adducts have been isolated.²⁻⁵ We report here the preparation, isolation, and initial investigation of salts of new complexes of this type in which *alkyl* groups are coordinated to the ring (1, R = CH_3 or $n-C_4H_9$).



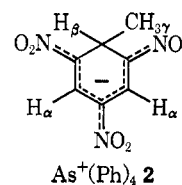
Alkyl-2,4,6-trinitrocyclohexadienate anions (1, R = CH_3 or $n-C_4H_9$) are readily prepared by adding TNB to solutions of the appropriate tetraalkylboron salts (see Experimental Section below). The visible spectra of these compounds are typical of TNB anion complexes (Table I).³ The positions and intensities of the bands are very similar in a variety of polar and non-polar solvents.

TABLE I
ABSORPTION MAXIMA FOR ACETONITRILE
SOLUTIONS OF COMPLEXES OF STRUCTURE 1

R	Cation	λ_1 , $m\mu$	ϵ_1^a , l. $mol^{-1} cm^{-1}$	λ_2 , $m\mu$	ϵ_2^a , l. $mol^{-1} cm^{-1}$
CH_3	$As^+(Ph)_4$	470	31,600	572	14,900
$n-C_4H_9$	$N^+(Me)_4$	474	31,800	568	14,800
$n-C_4H_9$	$As^+(Ph)_4$	474	31,500	568	14,700

^a Spectra obtained immediately after mixing; estimated errors <5% (see Experimental Section).

Nmr Spectra. A. Tetraphenylarsonium Methyl-2,4,6-trinitrocyclohexadienate (2).—The nmr spectrum



of an acetonitrile- d_3 solution of the compound obtained from the reaction of tetraphenylarsonium tetramethylboride and TNB is consistent with structure 2 (see Table II).⁶ The resonance frequencies and splitting

TABLE II
NMR CHEMICALS SHIFTS ($-\delta$) AND COUPLING CONSTANTS (cps)
FOR COMPOUNDS 2^a AND 3^a

Compd	H_α	H_β	H_γ	$J_{H_\alpha-H_\beta}$	$J_{H_\beta-H_\gamma}$	Cation protons
2	8.24	4.64	1.14	0.75 ± 0.05	6.2 ± 0.1	7.75^b
3	8.39	4.84	...	0.75 ± 0.05	4.2 ± 0.1	3.08^b

^a Salts are $\sim 0.1 M$ in acetonitrile- d_3 . A small impurity peak which was shown to be water was detected at 2.1 ppm. ^b Multiplet. ^c Butyl protons appear as a broad multiplet extending from ~ 0.8 to 1.9 ppm.

- (1) National Science Foundation Predoctoral Fellow, 1969–1970.
- (2) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969).
- (3) E. Bunce, A. R. Norris, and K. E. Russell, *Quart. Rev. Chem. Soc.*, **22**, 123 (1968).
- (4) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).
- (5) C. A. Fyfe, *Can. J. Chem.*, **46**, 3047 (1968).
- (6) Integrated intensities of the resonance absorptions agree with the proposed peak assignments.

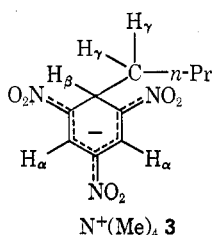
TABLE III
ANALYTICAL DATA^a

Compd	Found, %			Calcd, %			Mp, °C
	C	H	N	C	H	N	
N ⁺ (Me) ₄ (TNB-butyl) ⁻	48.46	6.87	15.99	48.83	7.02	16.27	206.5-207.5
As ⁺ (Ph) ₄ (TNB-butyl) ⁻	61.98	4.87	6.16	62.48	4.94	6.34	120-122
As ⁺ (Ph) ₄ (TNB-methyl) ⁻	61.24	4.42	6.95	60.89	4.29	6.87	166-167

^a Analyses were performed by Baron Consulting Co., Orange, Conn. 06477.

pattern observed for the ring protons are typical for "Meisenheimer" complexes.²⁻⁴ The fact that the γ -methyl protons are shifted slightly downfield from the methyl resonance frequency of methylcyclohexane is probably due to the anisotropy of the nearby NO₂ groups. The observed coupling constants and chemical shifts do not change significantly in other solvents. Addition of TNB to an acetonitrile-*d*₃ solution of **2** does not affect the nmr spectrum of the complex, indicating exchange of methyl anion between the complex and TNB must occur slowly (if at all!) at 40°.⁷

B. Tetramethylammonium Butyl-2,4,6-trinitrocyclohexadienate (3).—The nmr spectrum of this compound shows absorptions which can be assigned to the protons in **3** (see Table II).⁶ The proton resonances of



the anion do not change significantly when tetraphenylammonium is substituted for tetramethylammonium.

Ir Spectra.—The most significant features of the infrared spectrum of the (TNB-butyl)⁻ complex in deuteriochloroform are the presence of two very strong bands at 1219 and 1159 cm⁻¹ and the complete absence of bands at 1550 and 1345 cm⁻¹, the characteristic stretching frequencies of the NO₂ group in TNB.⁸ In analogy with Norris' investigation of the TNB-cyanide complex, we assign the intense bands at 1219 and 1159 cm⁻¹ to the antisymmetric and symmetric NO₂ stretching frequencies of the complex.⁸ This assignment is consistent with Norris' suggestion that the effect of delocalization of negative charge is to decrease the NO bond order, thus shifting the NO₂ stretching frequencies to lower energy.

Support for this point of view is provided by the following experiment: on acidification (HCl gas) of a deuteriochloroform solution of the (TNB-butyl)⁻ complex the purple color fades to yellow; new intense bands at 1545 and 1350 cm⁻¹ appear in the infrared spectrum of the acidified solution; and in addition, the previously observed NO₂ stretches are now completely absent. The nmr spectrum of the acidified solution indicates 2,4,6-trinitrobutylbenzene is a decomposition product. Similar color changes are obtained if the (TNB-methyl)⁻ complex is studied.

Experimental Section

Nmr spectra were recorded at 60 and 100 MHz on Varian spectrometers. Chemical shifts relative to internal tetramethyl-

(7) This result is quite general for "Meisenheimer" complexes.^{2,3}

(8) A. R. Norris and H. F. Shurvell, *Can. J. Chem.*, **47**, 4267 (1969).

silane were determined by the usual side-band techniques. Visible spectra were recorded using matched 1-cm quartz cells in a Cary 14 spectrometer, and infrared spectra were measured in 0.1-mm path length sodium chloride cells in a Beckman IR-12 spectrometer.

Preparation of Compounds.—The preparation of **3** is illustrative of the general synthetic procedure; a solution of TNB (0.60 g, 2.8 mmol) in 10 ml of acetone was added dropwise with stirring to a solution of tetramethylammonium tetrabutylboride⁹ (0.34 g, 1.1 mmol) in 10 ml of acetone under nitrogen. After addition was completed the resulting purple solution was stirred for 0.5 hr. Excess ether (~100 ml) was added to the reaction mixture, which was subsequently stored at 0° for 4 hr. The precipitated purple solid (0.29 g, 70%) was filtered, washed with ether, and recrystallized from an ethanol-ether mixture.

The preparation of the (TNB-methyl)⁻ complex was similar, except in order to achieve good yields it became necessary to stir the solutions for a much longer period (~12 hr) prior to the addition of ether.¹⁰

The salts appear to be relatively stable in air but were stored under nitrogen as a precautionary measure. The color of dilute solutions of the complexes fades in about 1 hr when they are exposed to light. Spectroscopic measurements were made on freshly prepared solutions and reproducibility was excellent. Analytical data are recorded in Table III.

Registry No.—**1**, R = *n*-C₄H₉, cation = As⁺(Ph)₄, 25448-31-1; **2**, 25448-32-2; **3**, 25448-33-3.

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(9) R. Damico, *J. Org. Chem.*, **29**, 1971 (1964).

(10) Trialkylboron compounds, which burn spontaneously in air, appear to be side products of these reactions. It is advisable to carry out these syntheses in a well-ventilated hood.

Mechanistic Aspects of the Wallach Transformation of Azoxybenzenes

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In strong sulfuric acid solutions, azoxybenzenes are converted to *p*-hydroxyazobenzenes in a process known as the Wallach transformation.² The exact dependence of the reaction rate on the acidity of the medium is unknown and appears to differ measurably for differently substituted azoxybenzenes,³ but it is evident that more than one proton is transferred to the azoxybenzene

(1) Deceased.

(2) E. Bunce in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968.

(3) D. Duffey and E. C. Hendley, *J. Org. Chem.*, **33**, 1918 (1968).