added. After 3 hr, the triethylamine hydrochloride was filtered from the solution and the filtrate was added dropwise to a solution of 5 g (0.12 mol) of aziridine in 25 ml of dimethylformamide at 5° with stirring. The reaction mixture was stirred for an additional 4 hr and then poured into ice water. The resulting white solid (5.7 g, 67%) was recrystallized from ethanol–water and was found to melt over the range 98–101°. The mass spectrum exhibited a molecular ion at *m/e* 190 (relative abundance, 35) and fragments at *m/e* 149 and 42 (relative abundances 100 and 11, respectively) which are assigned to the ions $(CH_3)_2NC_6H_4CO^+$ and $C_2H_4N^+$. The pmr spectrum of a 10% solution of the material in deuteriochloroform showed a sharp singlet at 2.28 ppm (relative area 4), a singlet at 3.00 ppm (relative area 6), and an apparent quartet centered at 7.4 ppm (relative area 4), downfield from tetramethylsilane. Prominent infrared bands at 1670, 1625, 1360, 1190, and 820 cm^{-1} were observed for the compound in a KBr matrix while absorptions at 1690, 1625, 1370, 1172, and 840 cm^{-1} were found with a 1% chloroform solution. These infrared features are quite consistent with the proposed acylaziridine structure.[4]

N-(*p*-Methoxybenzoyl)aziridine was prepared by the reaction of aziridine with anisoyl chloride. A stirred solution of 5 g (0.12 mol) of aziridine and 100 ml (0.72 mol) of triethylamine was treated with 17.1 g (0.1 mol) of anisoyl chloride in anhydrous ether over the course of 15 min. The mixture was stirred for a few minutes after the addition of the acid chloride was completed and then poured into water. The ether layer was washed with water and cooled until the crystallization occurred. The white product (mp 76–77°) was obtained in 80% yield. The pmr spectrum of the material showed sharp singlets at 2.32 (area 4) and 3.32 ppm (area 3) and a quartet at 7.1 ppm relative to TMS. The mass spectrum consisted of a molecular ion at *m/e* 177 (relative abundance 100) and peaks at *m/e* 135, 107, and 42 (relative abundances 40, 40, and 40, respectively) which are assigned to the ions $CH_3OC_6H_4CO^+$, $CH_3OC_6H_4^+$, and $C_2H_4N^+$, respectively. The infrared spectrum evidenced absorption at 1680, 1650, 1360, 1250, and 850 cm^{-1} in a KBr matrix and absorption at 1650, 1590, 1350, and 845 cm^{-1} in chloroform solution.

N-(*p*-Nitrobenzoyl)aziridine was prepared in a manner analogous to that used for the methoxy-substituted compound except that the product was insoluble in ether and was isolated by filtration in 60% yield. After recrystallization from acetone–water the pale yellow material melted over the range 170–172°. The nuclear magnetic resonance spectrum of the compound exhibited a singlet at 2.48 (area 4) and a broad singlet at 8.28 ppm (area 4) downfield from TMS. The mass spectrum showed a molecular ion at *m/e* 192 (relative abundance 36) and peaks at *m/e* 150 and 42 (relative abundance 100 and 56) which are assigned to the ions $NO_2C_6H_4CO^+$ and $C_2H_4N^+$, respectively. The infrared spectrum in a KBr matrix consisted of bands at 1675, 1620, 1355, 1228, and 807 cm^{-1} while in chloroform solution absorptions at 1648, 1620, 1355, 1150, and 810 cm^{-1} were noted. The pmr, ir, and mass spectral data were in complete accord with the assigned structure.

Cyclopropyl phenyl ketone-d_1 was prepared by dissolution of cyclopropyl phenyl ketone (Aldrich Chemical Co.) in a 2 *M* solution of NaOD in deuterium oxide. An equivalent volume of dioxane was added to help solubility and the mixture was heated under reflux for 2 or 3 days. The mixture was poured into water and extracted with ether. The ether extracts were washed with water, dried over sodium sulfate, and concentrated *in vacuo*. The residue was vacuum distilled to afford a product which showed essentially complete incorporation of deuterium into the position α to the carbonyl group, as determined by pmr spectroscopy.

The nuclear magnetic resonance spectra were taken with a JEOL C60-H spectrometer at 60 MHz and/or a Varian Associates HA-100 instrument at 100 MHz. Samples were 4–6% solute. Spectra of the cyclopropyl phenyl ketone-d_1 were recorded at 100 MHz with decoupling of the deuterium nucleus by means of an NMR Specialties, Inc., HD-60A spin decoupler. The standard variable-temperature accessory for each spectrometer was used; temperatures were determined with a Digitec Model 560 digital thermocouple and are believed to be accurate to at least 1°.

Registry No.—N-Benzoylaziridine, 7646-66-4; N-(*p*-dimethylaminobenzoyl)aziridine, 19614-27-8; N-(*p*-methoxybenzoyl)aziridine, 15269-50-8; N-(*p*-nitrobenzoyl)aziridine, 19614-29-0; IIId, 19614-30-3.

Acknowledgment.—This work was supported by Grant GM-14692 and Institutional Grant FR-07099 from the National Institutes of Health.

Proton Nuclear Magnetic Resonance, Infrared, and Electronic Spectral Properties of the Cyanide Ion–1,3,5-Trinitrobenzene σ Complex

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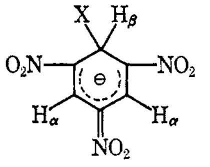
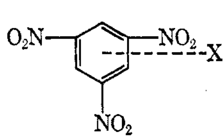
Received November 26, 1968

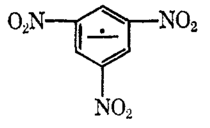
In recent years the ^1H nuclear magnetic resonance (nmr), infrared, and visible absorption spectra characteristic of the interactions of 1,3,5-trinitrobenzene and a variety of anions have been used to support the formulation of the resulting anionic species as σ complexes (I) rather than π complexes (II), radical anions (III), or aryl carbanions (IV).[1]



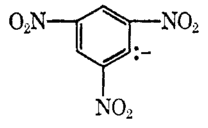
I



II



III



IV

X = OH, OCH_3, OC_2H_5, SO_3^-, CN, CH_2COCH_3, CH_3NH, and $C_5H_{10}N$

The spectra have been obtained, however, under quite different experimental conditions: nmr data from solutions approximately 0.50–1.0 *M* in both anion and nitro compound;[2-5] visible absorption data[6-8] from solutions whose concentration in either component may vary from 10^{-5} to 10^{-3} *M;* and infrared data, with one exception,[9] from the solids precipitated from concentrated solutions containing the two components.[10-13] As a result, there is some question whether the spectroscopic data refers to the same species in all cases.

We have now succeeded in obtaining nmr, infrared, and visible absorption data for the 1,3,5-trinitroben-

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zene–cyanide ion adduct in solutions of approximately the same concentration and here report some of our observations.

At −30°, deuteriochloroform solutions initially 0.39 *M* in 1,3,5-trinitrobenzene (TNB) and 0.35 *M* in tetraphenylarsonium cyanide (TPAC) possess, in addition to the multiplet in the 7.80-ppm region (external tetramethylsilane = 0.0 ppm) due to the tetraphenylarsonium ion (TPA^+), absorptions at 8.42 and 5.48 ppm (relative intensity 2:1). These resonance absorptions have been assigned previously to the H_α and H_β protons of the 1:1 σ complex I (X = CN).[14] The resonance absorption at 9.36 ppm which is characteristic of uncomplexed TNB in this system[14] is not observed in this case.

The infrared spectra (0.10-mm path length cells at −32°) of chloroform and deuteriochloroform solutions initially 0.39 *M* in TNB and 0.35 *M* in TPAC show absorptions due to TPA^+ [1490 (m), 1440 (m), 1080 (m), 995 (m), and 685 cm^{-1} (m)], uncomplexed TNB [3100 (vw), 1550–1555 (vw), and 1345 cm^{-1} (vw)], and new or *enhanced* absorptions at *1615* (m), 1495 (m), 1410–1400 (vw), 1235 (vs), 1190 (vs), 1050 (s), and *928* cm^{-1} (m). Possible new absorption bands in the 700–800-cm^{-1} region are not detected owing to strong solvent absorption in this region. The presence of very weak infrared absorptions at 3100, 1550, and 1345 cm^{-1} is in full accord with the absence of nmr absorption at 9.36 ppm.

Separate experiments establish that the new absorption bands at 1495, 1235, 1190, and 1050 cm^{-1} are characteristic of a 1,3,5-trinitrobenzene–cyanide ion complex of 1:1 stoichiometry and enable effective molar extinction coefficients to be obtained for each of these peaks.[15] Since the results of nmr spectroscopy suggest the predominant species in solution is σ complex I (X = CN), the infrared absorption bands at 1495, 1235, 1190, and 1050 cm^{-1} can be taken to be characteristic of this complex.

Deuteriochloroform solutions initially 0.042 *M* in TNB and 0.043 *M* in TPAC display, at −32°, infrared absorption bands similar to those observed in the more concentrated solutions. By employing the observed absorbance at 1235 cm^{-1} and the effective molar extinction coefficient of the 1235-cm^{-1} peak, the concentration of the σ complex is estimated to be 0.028 *M*.

The visible absorption spectrum (0.012-mm path length cell at −32°) of a deuteriochloroform solution initially 0.042 *M* in TNB and 0.043 *M* in TPAC possesses absorption maxima at 448 and 561 mμ with a ratio of absorbances at these two wavelengths of 1.81. This absorption pattern has been shown previously to be characteristic of a 1:1 1,3,5-trinitrobenzene–cyanide ion complex.[9] Employing the reported molar extinction coefficient of the 561-mμ peak in chloroform (ϵ 2.25×10^4 M^{-1} cm^{-1} at 25.3°)[9] the concentration of complex in the solution is calculated to be 0.030 *M*. This value is in good agreement with the calculated concentration of the complex obtained on the basis of infrared studies.

In conclusion we believe the major anionic species in chloroform and deuteriochloroform solutions containing TNB and TPAC in the concentration range 0.5–10^{-4} *M* is a σ complex of 1:1 stoichiometry. It is characterized by nmr resonance absorptions at 8.42 and 5.48 ppm (relative intensity 2:1), and infrared absorptions at 1495 (m), 1410–1400 (w), 1235 (s), 1190 (s), and 1050 cm^{-1} (m), and visible absorptions at 448 and 561 mμ (ϵ 4.05×10^4 and 2.25×10^4 M^{-1} cm^{-1}, respectively, at 25.3°). All of these absorptions may be used to obtain quantitative information on the extent of complex formation under given reaction conditions.

Simultaneous measurements of this type are now being extended to the 1-Y-2,4,6-trinitrobenzene–cyanide ion interactions.

Registry No.—I, 19614-50-7.

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Reactions of *t*-Butyl Hypohalites with Carbanions and Alkoxides[1]

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Hydrogen peroxide and its organic derivatives react rapidly with a variety of nucleophiles,[3] and, as an example, *t*-butyl peroxy esters react with Grignard reagents by nucleophilic displacement on oxygen to give *t*-butyl ethers in satisfactory yields.[4] With *t*-butyl hypohalites, nucleophilic displacement might occur on either halogen or oxygen, and in the latter case carbanionoid reagents would again yield ethers. We have now investigated the reaction of *t*-butyl hypochlorite with a number of organometallic compounds, Table I, and find that, not surprisingly, reaction on halogen is in fact the predominant, if not exclusive, path; thus the reaction, if informative, is of little synthetic interest.

TABLE I

REACTIONS OF *t*-BUTYL HYPOCHLORITE WITH ORGANOMETALLIC REAGENTS[a]

Reagent	Products
RLi (from RCl)	RCl
RLi (from RBr)	RCl, RBr
RMgCl (from RLi)	RCl
RMgBr	RCl (50%), RBr (25%), RO-*t*-Bu (trace)
R_2Zn (from RMgBr)	RCl, RBr, RO-*t*-Bu (0.5%)
R_2Cd (from RMgBr)	RCl, RBr, RO-*t*-Bu (1%)
R_2Hg	RCl, acetone, *t*-butyl alcohol[b]
R_4Sn	RCl[c]

[a] R = phenyl. [b] On irradiation, little or no reaction in dark. [c] After 14 days, very slow reaction.

The reaction of *t*-butyl hypohalites with the *t*-butoxide anion is more interesting. Here displacement of halogen is simply an identity reaction regenerating

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[1] Taken from the Ph.D. dissertation of J. Kjellgren, Columbia University, 1966. Support of this work by the National Science Foundation is gratefully acknowledged.

[2] National Science Foundation Fellow, 1962–1964; Union Carbide Corp. Fellow, 1964–1965.

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