and 5 mmol (0.85 g) of silver nitrate were mixed with 35 mL of dry acetonitrile. Into this solution was added 4.5 mL of saturated boron trifluoride/acetonitrile solution under a dry nitrogen atmosphere. The reaction mixture was vigorously stirred, and the temperature was kept constant at 25 °C during the reaction. The reaction time was generally 5 h (10 h, for halobenzenes). The reaction solution was then quenched with ice–water, extracted with ether, washed with 5% sodium bicarbonate solution, dried over magnesium sulfate, concentrated, and analyzed by gas–liquid chromatography.

Analytical Procedure. The analyses of all products were carried out by gas–liquid chromatography with a Varian Associates Model 3700 gas chromatograph equipped with a hydrogen flame ionization detector and with a 25 m × 0.25 mm i.d. OV-101 glass capillary column with helium as a carrier gas. Peak areas were measured with a Varian CDS III electronic integrator. The results of competitive nitrations are the average of three independent reactions. The average deviation of the substrate selectivities was less than 1.0, and that of isomer distribution was ±1.096.

Procedure for Nitration of *p*-Xylene. *p*-Xylene (10.6 g, 0.1 mol) and silver nitrate (1.7 g, 0.01 mol) were mixed with 50 mL of dry acetonitrile. Into this solution was added 5 mL of boron trifluoride/acetonitrile solution. The reaction mixture was vigorously stirred, and the temperature was kept constant at 25 °C during the reaction. After an 18-h reaction time, the reaction solution was quenched with ice–water, extracted with ether, washed with 5% of sodium bicarbonate solution, dried over magnesium sulfate, concentrated, and distilled under reduced pressure; yield 1.39 g (91.4%).

Mononitration of Polymethylbenzenes. Equimolar amounts of polymethylbenzenes and silver nitrate were mixed with a sufficient amount of acetonitrile to give a clear solution. Into this solution was added 4 mL of boron trifluoride/acetonitrile solution at 0 °C. The resulting mixture was then kept at 25 °C for 8 h. After the usual workup, mononitrated products were obtained which were further purified by recrystallization (ethanol or ethanol/petroleum ether) and identified by physical and spectral as well as gas chromatographic characteristics.

Acknowledgment. Support of our work by the U.S. Army Office of Research, Durham, NC, is gratefully acknowledged.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; ethylbenzene, 100-41-4; isopropylbenzene, 98-82-8; *n*-propylbenzene, 103-65-1; *tert*-butylbenzene, 98-06-6; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 1,2,3-trimethylbenzene, 526-73-8; 1,2,4-trimethylbenzene, 95-63-6; 1,3,5-trimethylbenzene, 108-67-8; 1,2,3,4-tetramethylbenzene, 488-23-3; 1,2,4,5-tetramethylbenzene, 95-93-2; anisole, 100-66-3; fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; iodobenzene, 591-50-4; 1,2,3,4,5-pentamethylbenzene, 700-12-9; 1,2,3,5-tetramethylbenzene, 527-53-7; silver nitrate, 7761-88-8; acetonitrile, 75-05-8; BF_3, 7637-07-2.

Reactivity of Carbon Acids toward 4,6-Dinitrobenzofuroxan. Studies of Keto–Enol Equilibria and Diastereoisomerism in Carbon-Bonded Anionic σ Complexes

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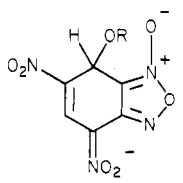
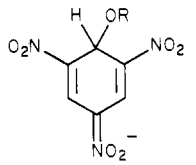
4,6-Dinitrobenzofuroxan (DNBF) reacts with monoketones and β-diketones in dimethyl sulfoxide solution to give carbon-bonded σ adducts. As shown by NMR, the reactions occur in the absence of any added base, emphasizing the highly electrophilic character of this heterocycle. With monoketones only ketonic adducts are formed, while with β-diketones both enolic and/or ketonic σ complexes are observed. The presence of two chiral centers in the DNBF–cyclopentanone adduct enabled the first characterization of two diastereomeric σ complexes. The structure of both kinetically and thermodynamically favored diastereomers are tentatively assigned on the basis of the geometry of the transition states leading to them. It is also shown that enolic σ adducts are formed from the reaction of 1,3,5-trinitrobenzene with β-diketones in the presence of base.

4,6-Dinitrobenzofuroxan is a much stronger electrophile than polynitro aromatic compounds like trinitrobenzene (TNB), 1,3,6,8-tetranitronaphthalene (TNN), and 1,2,3,5-tetranitrobenzene (TTNB). Thus, it reacts very easily with water or methanol in aqueous or methanolic solution, in the absence of any added hydroxide or methoxide ion, to give the σ adducts 1.[1] Such a reaction does not occur, even to a small extent, in the formation of hydroxyl or methoxyl adducts 2–4 from TNB, TNN, and TTNB. These are the most electrophilic benzenes known to date.[2–6] This remarkable behavior of 4,6-dinitro-



1a, R = H
b, R = CH_3



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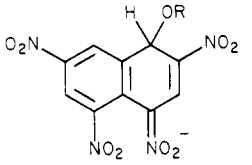

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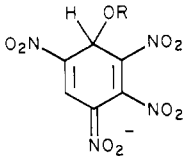

4

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Table I. NMR Parameters[a] of the DNBF-Monoketone σ Adducts (Solvent Me_2SO-d_6)

σ adducts	shift H_5	H_7	$H_{1'}$	$CH_{3(3')}$	$^3J_{1',7}$	J
5	8.48	4.44 (X)	3.22 (A) 3.02 (B)	1.99	4.15 ($^3J_{AX}$) 4.15 ($^3J_{BX}$)	−17.7 ($^2J_{AB}$)
6a (K)	8.61	4.79	2.65		2.0	
6b (T)	8.66	4.60	2.51		1.3	

[a] Shifts (δ) in parts per million from internal Me_4Si. J values are in hertz. The probe temperature was 32 °C.

benzofuroxan (DNBF) is also evidenced by the much higher stability of the adduct **1a**, compared with that of adducts **2a**–**4a** (R = H). For example, in aqueous solution the $pK_a^{H_2O}$ for the formation of **1** is 3.75 at 25 °C as compared with $pK_a^{H_2O}$ values of 13.43, 9.96, and 9.62 for the formation of **2a**–**4a**, respectively.[2,3,5,6]

Surprisingly, the reactivity of DNBF toward other nucleophiles has not been studied. In this paper, we report the first NMR evidence that DNBF in dimethyl sulfoxide solution reacts with various ketones *in the absence of added base* to give carbon–bonded σ adducts. Due to the nonsymmetric nature of DNBF, this study provides the first substantial evidence for diastereomeric σ adducts. Also noteworthy is the observation of σ adducts formed from some β-diketones existing in the enol form. Such enolic complexes have been also characterized in the reaction of TNB with β-diketones in the presence of 1 equiv of base. These complexes are in fact precursors of the previously reported bicyclic adducts which are immediately formed if an excess of base is used.[7-10] This study documents the existence of these complexes, which previously have been the subject of speculative discussion.

It should be pointed out that complexes of DNBF are isolable as their potassium salts, and we have in fact isolated some of the ketonic adducts described here by adding KOAc or KF to the solution [i.e., 11 + KOAc → K^+,11 (ppt) + HOAc]. Such adducts are *highly explosive and shock sensitive*, and after explosions in the melting point apparatus, the mass spectrometer, and during isolation procedures, we abandoned further attempts at isolation or elemental analysis. The NMR spectra show no evidence for any reactions except complex formation. A word of caution to anyone attempting to work with such materials: keep them in solution!

Results

The reactivity of DNBF toward the following ketones was investigated: acetone, cyclopentanone, cyclopentanedione, 2,4-pentanedione, and 3-methyl-2,4-pentanedione. The course of the reaction was examined by following the evolution of ^1H NMR spectra as a function of time. A similar procedure was used to study the reactions of cyclopentanedione and 2,4-pentanedione with TNB, but complex formation was observed only after addition of NEt_3(KOMe) (1 equiv).

The numbering of the carbons of the ketonic moieties was chosen to allow a direct comparison of the NMR parameters in the various adducts. In all cases, $C_{1'}$ denotes the carbon bonded to the sp^3 carbon of DNBF (C_7) and TNB (C_1).

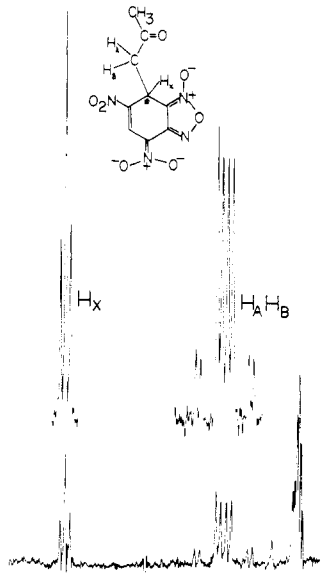
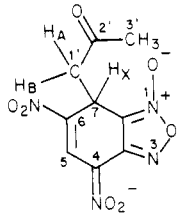


Figure 1. Partial ^1H NMR spectrum of the DNBF–acetone σ adduct **5** (ABX part).

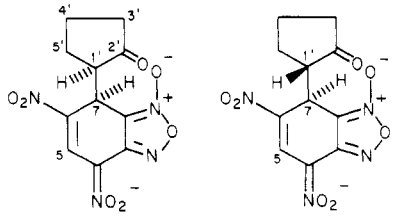
Reaction of DNBF with Monoketones. Adding an equivalent amount of acetone to a solution of DNBF in Me_2SO-d_6 resulted in the immediate formation of the adduct **5**. Owing to chirality of the tetrahedral ring carbon



5

C_7, the geminal protons are diastereotopic and appear as the AB part of an ABX system, which is particularly well resolved (Figure 1). A second-order analysis gives the parameters reported in Table I.

Reaction of cyclopentanone with DNBF must result in the formation of two chiral centers and the possibility for the two diastereomeric complexes **6a** and **6b** arises (only one enantiomer for each is shown).



6a (K) 6b (T)

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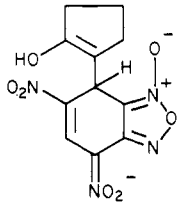
(10) Strauss, M. J.; Bard, R.; Schran, H. *J. Org. Chem.* **1973**, *38*, 3394.

Table II. NMR Parameters[a] of the DNBF-β-Diketone σ Adducts (Solvent Me_2SO-d_6)

σ adducts	shift H_5	H_7	$H_{1'}$	CH_2 (3'/4')	CH_3 (3'/3'')	CH_3 (4')	OH	$^3J_{1',7}$	J
9a,b[b]	8.60	5.20		2.36			10.36		0.3 ($^4J_{5,7}$)
11[c]	8.57	5.07	4.64		2.31/2.08			2.6	0.3 ($^4J_{1',3'/3''}$)
12a,b[c]	8.62	5.49			2.44/1.84		11.78		
13[b]	8.60	5.21			2.23/2.07	1.22			0.5 ($^4J_{5,7}$)

[a] Shifts (δ) in parts per million from internal Me_4Si. J values are in hertz. [b] Determined at probe temperature (32 °C). [c] Determined at 23 °C.

In agreement with this expectation, NMR spectra exhibited two sets of signals, the relative intensities of which changed with time. When the sample was allowed to stand for several days, the resonances of the kinetically favored diastereomer K decreased while those of the thermodynamically favored diastereomer T increased (Table II). After 1 week, T became the major species in the solution. For each complex, H_7 appeared as a clear doublet, confirming the absence of the enolic form **7**. Irradiation of $H_{1'}$ in **6a** or **6b** resulted in collapse of the corresponding H_7 doublet in each case. K and T are probably **6a** and **6b**, respectively (vide infra).



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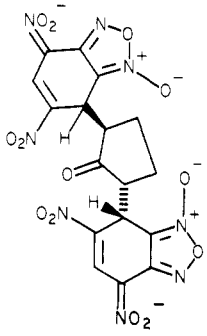
Interestingly, in an excess of DNBF over cyclopentanone, a third H_7 doublet (δ 4.81, J = 1.9 Hz) slowly appeared at the expense of those belonging to **6a** and **6b** (Figure 2). Irradiation of the $H_{1'}$ signal of the kinetically preferred diastereomer K resulted in a simultaneous collapse of the H_7 doublets in K and this new species, both of which therefore have similar $H_{1'}$ chemical shifts (Figure 3). These results are consistent with the formation of a diadduct, which may have a cis or trans structure. The trans structure **8** is proposed because of extreme steric



8

compression in the cis isomer. Evidence for the formation of such a diadduct has been previously obtained in reaction of dibenzyl ketone with a large excess of TNB.[10]

Reaction of DNBF with β-Diketones. Addition of 1,3-cyclopentanedione ($pK_a^{H_2O}$ = 4.5[11]) to a Me_2SO-d_6 solution of DNBF immediately yielded the stable enolic adduct **9**, as evidenced by the ^1H NMR spectra (Table II) which showed the absence of a large $^3J_{1',7}$ coupling constant and the presence of a OH signal at low field (δ 10.36).

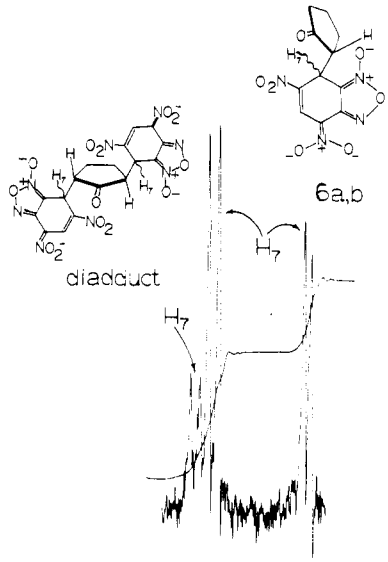
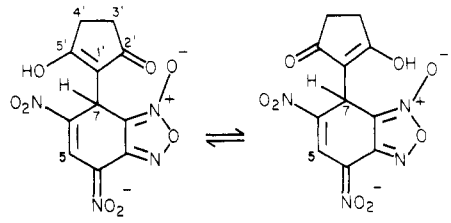
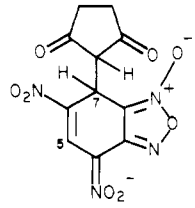


Figure 2. Partial ^1H NMR spectrum of the DNBF–cyclopentanone reaction mixture (excess DNBF): H_7 doublets of the diadduct **8** and kinetic (**6a**) and thermodynamic (**6b**) diastereomeric monoadducts.

Further support for **9** was the broad singlet at 2.36 ppm observed for the methylene protons on $C_{3'}$ and $C_{4'}$, which resulted from rapid tautomeric equilibrium between **9a** and **9b** at the probe temperature (32 °C). No trace of the ketonic complex **10** could be detected in the ^1H NMR spectrum, even at the beginning of the reaction.



9a **9b**



10

Addition of the less acidic 2,4-pentanedione ($pK_a^{H_2O} \approx 9$[12-14]) resulted in an interesting sequence of reactions. The

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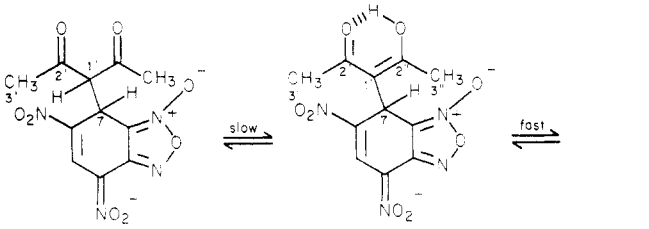
Table III. NMR Parameters[a] of the TNB-β-Diketone σ Adducts (Solvent Me_2SO-d_6)

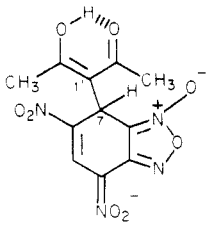
σ adducts	shift					
	$H_{3/5}$	H_1	CH_2 (3'/4')	CH_3 (3')	CH_3 (3")	OH
14a,b[b]	8.05	5.29	2.21			8.52
15a,b[c]	8.32	5.78		2.56	1.91[d]	17.28

[a] Shift (δ) in parts per million from internal Me_4Si. [b] Determined at probe temperature (32 °C). [c] Determined at 23 °C. The methyl 3' and 3" signals coalesce at about 30 °C. [d] Double-resonance experiments show the existence of a long-range coupling constant, $^4J_{CH_3(3'')\text{-}C\text{-}OH}$, involving the high-field methyl (3") bonded to the enolic double bond.

ketonic σ complex **11** was initially observed by NMR. This then underwent a slow and partial conversion into the enolic form **12**. While H_7 gave a doublet in **11** ($^3J_{1',7}$ = 2.6 Hz), it became a singlet in **12** (Table II).



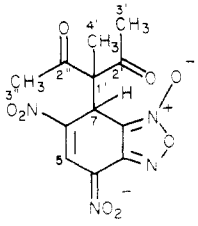
11 **12a**



12b

In the ketonic adduct **11**, chirality at C_7 results in nonequivalence of the methyl groups of the diketone moiety. Evidence for a fast equilibrium between the two tautomers **12a** and **12b** comes from the observation of two broad singlets for the methyl resonances. These two signals become sharper and sharper with decreasing temperature [down to −40 °C in a 20:80 (v/v) MeOD/Me_2SO-d_6 mixture]. After complete equilibration of the reaction at 32 °C (~2 h), **11** and **12** were present in a ratio of 30:70, essentially identical with the ratio of keto and enol forms of 2,4-pentanedione itself in Me_2SO-d_6 at the same temperature.

As expected, 3-methyl-2,4-pentanedione ($pK_a^{H_2O}$ = 11.06[15]) gave only the ketonic adduct **13** which has no enolizable hydrogen. Again in agreement with chirality at C_7, the two ketonic methyl groups in **13** are nonequivalent (Table II).



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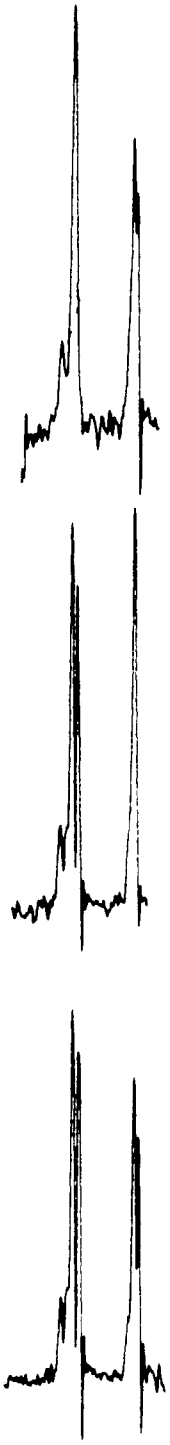
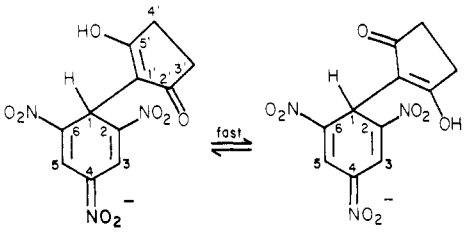


Figure 3. Partial ^1H NMR spectrum of the DNBF–cyclopentanone reaction mixture (without excess DNBF): H_7 doublets of **8** (in small proportions), **6a** (K), and **6b** (T). Upper traces: decoupling experiments with successive irradiation of $H_{1'}$ of **6b**(T) and of **6a**(K).

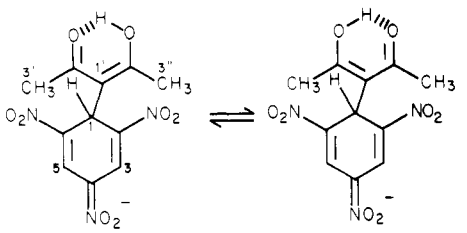
Reaction of TNB with β-Diketones. In the presence of triethylamine, 1,3-cyclopentanedione added to TNB to give exclusively the enolic complex **14**, as evidenced by the ^1H NMR spectra which showed the absence of any strong $^3J_{1,1'}$ coupling constant and the presence of an OH signal (Table III). The equilibrium between the two tautomers **14a** and **14b** was fast on the NMR time scale at the probe temperature (32 °C), as shown by the observation of a singlet for the methylene protons on $C_{3'}$ and $C_{4'}$.

Only upon addition of a base (1 equiv of KOMe) to a solution of TNB and 2,4-pentanedione in Me_2SO-d_6 did reaction occur to give the enolic complex **15** (Table III).



14a 14b

At the probe temperature, only a broad absorption was observed for the methyl resonances of **15**. This is in line with the absence of chirality at the sp^3 carbon C_1 and shows that the tautomeric equilibrium **15a** ⇄ **15b** is fast on the



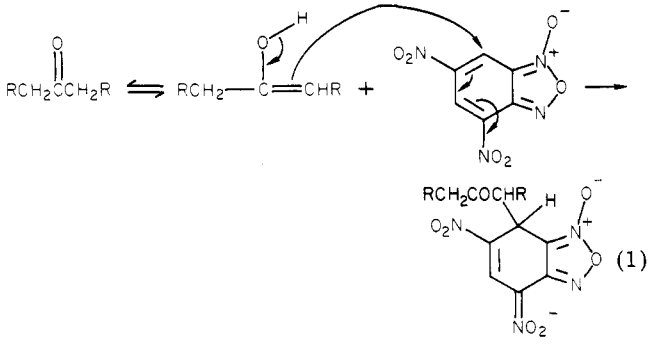
15a 15b

NMR time scale. Decreasing the temperature (23 °C) resulted in two signals which became sharper on further cooling whereas at higher temperature (about 30 °C) they coalesced.

Double-resonance experiments were performed at 23 °C. Irradiation of the low-field methyl signal (δ 2.56) produced no change in the OH resonance, whereas irradiation of the high-field methyl signal (δ 1.91) resulted in a sharper OH resonance. This implies the existence of a long-range coupling constant, $^4J_{H_3C-OH}$, involving the high-field methyl bonded to the enolic double bond. It further indicates a coplanar zig-zag structure of this moiety, in accordance with an intramolecular H bonding. Furthermore, the assignment deduced for the methyl signals is in agreement with the chemical shifts observed for the methyl groups in the keto (δ 2.17) and enol (δ 2.02) forms of the parent 2,4-pentanedione (cf. Experimental Section).

Discussion

The fact that ketones of very low acidity like acetone and cyclopentanone react with DNBF in the absence of any added base emphasizes the highly electrophilic character of this heterocycle. Such reactions must result from attack of equilibrium concentrations of enol to give a ketonic carbon-bonded σ adduct (eq 1). For the most acidic

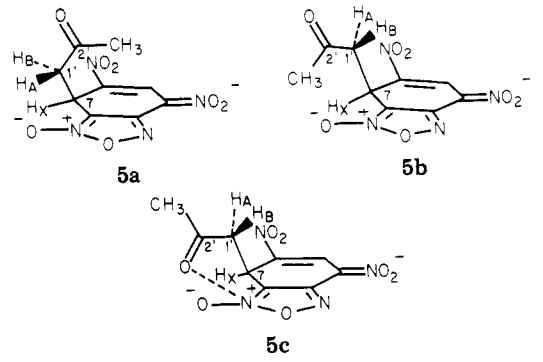


(1)

β-diketones, which exist mainly in the enol form in dimethyl sulfoxide, the mechanism depicted in eq 1 is probably reasonable. However, adduct formation resulting from attack of the enolate generated by ionization of the enol cannot be excluded. Even though equilibrium concentrations of such anionic species are exceedingly small, they should have a much higher reactivity than the corresponding enols. It is thus possible that enolate attack is kinetically favored over enol attack, but the two pathways cannot be distinguished. When basic media are used, as for TNB complexes,[7-10] enolate attack is the only reasonable pathway. In both cases, a ketonic complex is initially formed, and subsequent enolization can occur.

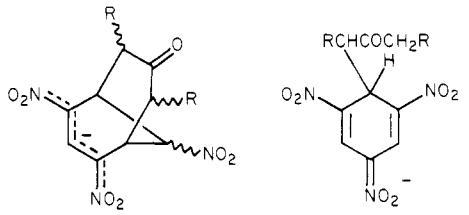
Though not yet estimated quantitatively due to the difficulty of isolating solid salts, the stability of the DNBF–ketone σ adducts is certainly very high. This can be anticipated since the analogous TNB adducts, which are known to be very stable, cannot be formed under such mild conditions.[7-10]

The NMR parameters obtained for the DNBF–acetone adduct **5** allows some speculation about its preferred conformation in solution. The equality of both vicinal coupling constants $^3J_{AX} = {}^3J_{BX} = 4.1_5$ suggests that the two dihedral angles H_A–C_1–C_7–H_X and H_B–C_1–C_7–H_X are close to 60° or 120°. This favors bisected conformations such as **5a**, **5b**, or **5c**. Examination of molecular models



5a 5b 5c

shows substantial interaction between the acetyl methyl group and furoxan N^+–O^- and 6-NO_2 functions in **5b**. In addition, this conformation is completely eclipsed. Rotation about the $C_{1'}$–$C_{2'}$ bond can give conformer **5c**, however, which may be stabilized by the C=O···N^+—O^- interaction. Interestingly, it should be noted that conformations like **5a** have been proposed as a prerequisite for bridging to structures like **16** in complexes of TNB.[7] It is difficult to definitively assign a preferred conformation, but we favor **5a** or **5c**.



16 17

Proton nonequivalence was previously reported in TNB complexes like **17** with chiral centers in the ketonic moiety.[20] Chirality in this instance makes the anionic ring protons nonequivalent, but the effect is much smaller than in **5** where the chiral center is closer to the diastereotopic protons.

On the basis of the unique character of the cyclopentanone moiety in anionic σ-complexes,[16,17] reasonable speculations can be made about the structures of the two observed diastereomeric DNBF complexes K and T. Both

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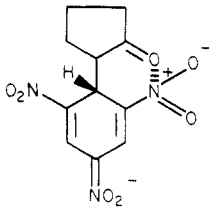
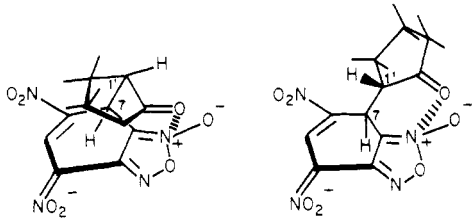
(17) Wulff, C. A.; Murphy, R. M.; Strauss, M. J. *J. Org. Chem.* **1975**, *40*, 1499.

thermodynamic and ^{13}C NMR studies, as well as studies of the acid-catalyzed decomposition of such complexes, have shown that a preferred and stabilized conformation for cyclopentanone complexes with TNB is one where the carbonyl oxygen is oriented close to the positive nitrogen of an adjacent nitro group, i.e., 18.[16-18] A similar orien-



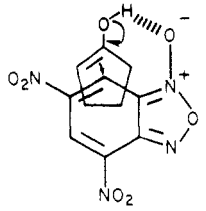
18

tational preference might be expected for 6, between the more highly positive furoxan nitrogen and the carbonyl oxygen. Such an interaction in 6 results in the conformations shown (6a,b). We suggest that 6a is formed



6a 6b

initially as a kinetically favored product (diastereomer K) because there is more effective π overlap of enol and DNBF in the transition state than in the transition state leading to 6b. In addition a favorable H-bonding interaction of the enolic OH and furoxan oxygen might be important (6a (K)). Once formed however, a C=O···



6a (K)

N^+—O^- interaction in the complex orients the cyclopentanone methylenes over the DNBF in 6a (vide supra). Such an interaction does not occur in 6b (diastereomer T) which may therefore be thermodynamically favored. The equilibration of 6a and 6b probably occurs via the enolic form 7. The structural assignments for 6a and 6b are supported by the 19-Hz upfield shift for H_7 and the 14-Hz upfield shift for $H_{1'}$ on going from 6a to 6b. It should be noted that in the favored conformation for 6b, $H_{1'}$ occupies a position over the delocalized anionic ring whereas in 6a the favored conformation places it anti to this ring. In addition, a stronger C=O···N^+—O^- interaction in 6b than in 6a might diminish the electronegative effect of the furoxan nitrogen. This could result in a slight H_7 upfield shift in going from 6a to 6b.

σ adducts from DNBF and diketones are primarily enolic. However, the conditions for their formation are dependent upon the nature of the diketone. In the case of 1,3-cyclopentanedione, the ketonic complex 10 cannot be detected by NMR. The observation of only the enol form 9 implies that the rate of enolization of 10 is greater than its rate of formation from parent enol attack on DNBF. A different situation holds in the DNBF–2,4-pentanedione adduct where the keto form 11 is first observed. Here, enolization of 11 is the rate-determining step. A noteworthy feature is that the enol content is the same as in the parent diketone. Thus the negatively charged DNBF moiety has apparently no effect on the keto–enol equilibrium. This is surprising since this moiety is known to have an appreciable electron-withdrawing character.[1] In the TNB complexes 14 and 15, the keto–enol equilibrium is shifted toward the enol forms due to the presence of base in the solutions.

Conclusion

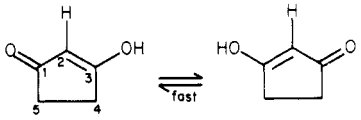
The powerful electrophilic character of 4,6-dinitrobenzofuroxan is emphasized by its unusually high reactivity toward weak carbon acids such as ketones in the absence of added base. The diminished aromaticity of DNBF (relative to TNB) together with the strong electron-withdrawing effect of the annelated furoxan ring[1,21-25] are probably responsible for this behavior. It is in striking contrast with that of polynitro aromatics like 1,3,5-trinitrobenzene. The mechanisms of the reactions involve attack of the enol forms of the ketones to give keto adducts which rapidly enolize (in the case of β-diketones).

Experimental Section

3-Methyl-2,4-pentanedione was prepared from the reaction of methyl iodide with the sodium salt of 2,4-pentanedione according to the method described by Perkin:[26] Eb_{20mmHg} = 74–75 °C. All the other ketones were commercial products which have been purified by standard procedures. 1,3,5-trinitrobenzene (Eastman Kodak) was recrystallized two times from methanol; mp, 123 °C. 4,6-Dinitrobenzofuroxan was prepared by the procedure of Drost;[27] mp, 172 °C.

^1H NMR spectra were recorded on a Varian XL-100-12 WG spectrometer. Chemical shifts were measured with Me_4Si as an internal reference.

Spectra of the parent β-diketones dissolved in Me_2SO-d_6 were examined at 100 or 60 MHz (Varian A 60). Only the enol form of cyclopentanedione was observed (eq 2). Keto and enol forms



(2)

H_2, δ 5.10; $C(4,5)H_2$, δ 2.38; OH, δ 11.13

of 2,4-pentanedione were observed in the ratio 30/70. Keto: CH_3, δ 2.17; CH_2, δ 3.70. Enol: CH_3, δ 2.02; =CH, δ 5.64; OH, δ 14.72. Keto and enol forms of 3-methyl-2,4-pentanedione were observed in the ratio 78/22. Keto: 3-CH_3, δ 1.16 (d); $C(1,5)H_3$, δ 2.15; C(3)H, δ 3.86 (q); J = 7.06 Hz. Enol: 3-CH_3, δ 1.80; $C(1,5)H_3$, δ 2.09; OH

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δ 16.46. In Me_2SO-d_6 solution, two doublets were observed for DNBF: H_5, δ 9.19; H_7, δ 8.92; $^4J_{5,7}$ = 1.8 Hz. The singlet of TNB was at δ 9.13.

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Registry No. 5, 77902-62-6; **6a**, 77902-63-7; **6b**, 77902-64-8; **9a/9b**, 77902-65-9; **11**, 77902-66-0; **12a/12b**, 77902-67-1; **13**, 77902-68-2; **14a/14b**, 77902-69-3; **15a/15b**, 77902-70-6; 4,6-dinitrobenzofuroxan, 5128-28-9; 3-hydroxycyclopent-2-en-1-one, 5870-62-2; 2,4-pentanedione, 123-54-6; 4-hydroxypent-3-en-2-one, 1522-20-9; 3-methyl-2,4-pentanedione, 815-57-6; 4-hydroxy-3-methyl-3-penten-2-one, 1522-25-4.

Comparative Study of the Water-Catalyzed Hydrolysis of [(*p*-Nitrophenyl)sulfonyl]methyl Perchlorate in 1,4-Dioxane–Water and in 1,3-Dioxane–Water

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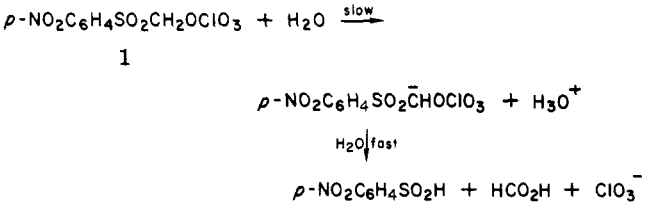
Pseudo-first-order rate constants (k_{obsd}) and thermodynamic activation parameters have been compared for the water-catalyzed hydrolysis of [(*p*-nitrophenyl)sulfonyl]methyl perchlorate (1) in 1,4-dioxane–water and in 1,3-dioxane–water. Characteristic differences in the kinetic basicities of both reaction media are only observed below n_{H_2O} = 0.80 and most likely reflect the specific hydrogen bonding interactions between water and the organic cosolvent. The structural properties of both aqueous binaries are critically discussed, and it is concluded that the maxima in k_{obsd} at about n_{H_2O} = 0.80 in both solvent mixtures do not reflect an enhanced degree of water structure at this solvent composition.

The wide range of dielectric constants (ε = 2.2–78, 25 °C) that can be attained in mixtures of 1,4-dioxane with water, together with their excellent solubilizing properties, seem to make them ideal media for synthetic and mechanistic studies in organic chemistry. However, the 1,4-dioxane–water system exhibits pronounced deviations from ideal behavior in the thermodynamic sense,[1] which especially complicate mechanistic investigations. In the water-rich region, the anomalies have been frequently attributed[2] to "water-structure effects". Unfortunately, however, there is strong controversy in the literature concerning the interpretation of kinetic solvent effects in this popular mixed aqueous system since in different studies, 1,4-dioxane has been characterized either as a water-structure breaker or as a water-structure promotor.[3] Structure-making properties have been claimed on the basis of ultrasonic absorption measurements,[4] infrared, raman,[5,6] and NMR spectroscopic studies,[7] and dielectric relaxation measurements.[8] The results of these studies were interpreted in terms of structure promotion upon the addition of 1,4-dioxane to water down to a mole fraction of water (n_{H_2O}) of ca. 0.8. By contrast, several properties of the 1,4-dioxane–water system have been rationalized by assuming a destabilizing effect of the organic cosolvent on the three-dimensional hydrogen bond regime. Strong evidence for this idea is provided by the structural part of the temperature of maximum density (TMD) depression[9] and by studies of the solubility of argon in 1,4-dioxane–water mixtures.[10] Evidence in favor of structure breaking is also provided by X-ray diffraction studies,[11] the effect of pressure on density,[12] apparent molar heat capacities,[13] partial molal excess heat capacities,[14] excess molar volumes,[15] enthalpies of transfer of slightly soluble salts,[16] and the enthalpies of hydrophobic interaction in combination with partial molar volumes.[17]

Described herein is a comparative study of the rates and thermodynamic activation parameters of the water-catalyzed hydrolysis of [(*p*-nitrophenyl)sulfonyl]methyl perchlorate (1) in 1,4-dioxane–water and 1,3-dioxane–water.



The mechanism of this reaction involves general-base catalysis by water, implying rate-determining deprotonation at the α-sulfonyl carbon.[18] In previous studies, the process

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