

Nitration of Triptycene

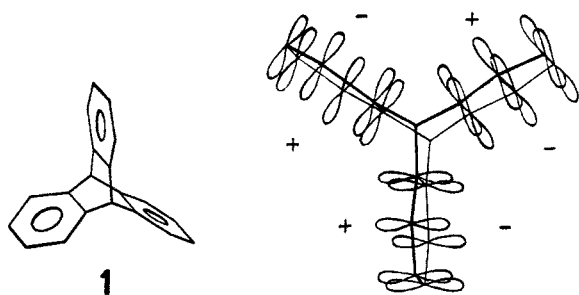
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Triptycene is mononitrated predominantly in the β position to give 2-nitrotriptycene, which, in turn, is nitrated to give a mixture of 2,6- and 2,7-dinitrotriptycenes. The relative rates for the nitration of triptycene and 9,10-dihydro-9,10-ethanoanthracene indicate that no transannular resonance or polarization effects are operative between the aromatic rings of the triptycene system. The relative rates for the first and second nitrations of triptycene give a measure of the inductive effects operating in the triptycene system.

The possibility that transannular interactions may operate in the triptycene system (1) has been suggested and investigated on a number of occasions.¹⁻⁵ The results of ultraviolet (uv) and nuclear magnetic resonance (nmr) studies have been either negative (with respect to the operation of transannular interactions) or nondefinitive. In two special types of triptycene systems,^{6,7} evidence for transannular interactions has been obtained; however, these systems are modified triptycenes and the conclusions are based on the energy differences between ground and excited states. The transannular interactions may simply be occurring in the excited states. It should be noted that any transannular resonance effects which might be operative in the triptycene system cannot "circulate around and around" because of unfavorable orbital overlap, as is illustrated in the diagram below showing a top view of the triptycene system. A discontinuity always exists

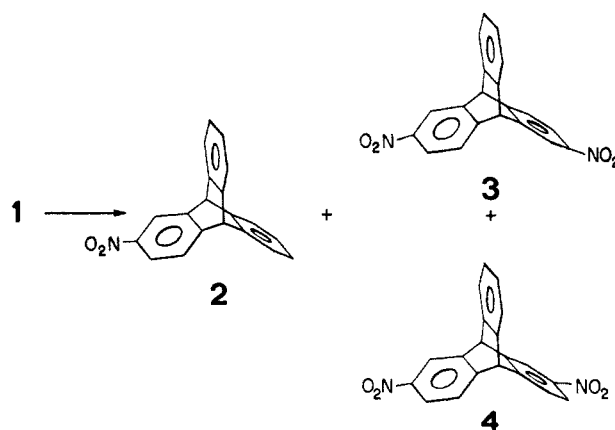


between two of the rings for the lowest energy Hückel molecular orbital (HMO).

Transannular interactions for biphenylene⁸ and bicyclo[2.2.2]octadiene⁹ have been demonstrated; the nature of these systems and the products formed in various reactions support transannular resonance effects while ruling out steric effects.

To understand better how effects are transmitted between the rings of the triptycene system, we studied the nitration of triptycene with respect to products

formed and relative rates of mono- and dinitration. The nitration of triptycene in acetic anhydride with 1-2 equiv of nitric acid in acetic acid gives a mixture of products: recovered triptycene, 2-nitrotriptycene (2), 2,6-dinitrotriptycene (3), and 2,7-dinitrotriptycene (4).



The composition of product mixtures was determined by nmr and is shown in Table I. The bridgehead proton absorption was convenient to follow and gives a direct value for the proportion of each of the materials present. 2-Nitrotriptycene and 2,6-dinitrotriptycene were isolated from the reaction mixture by chromatography and recrystallization. 2-Nitrotriptycene had previously been prepared by the reaction of 4-nitrobenzylne with anthracene.¹⁰ The following characteristics of the nitration of triptycene should be noted. (1) 2-Nitrotriptycene is not formed exclusively before dinitration occurs; *i.e.*, the discrimination of a nitrating species between starting material, triptycene, and mononitrated product, 2-nitrotriptycene, is not high. (2) Almost exclusive β nitration occurs; only 2.3% 1-nitrotriptycene (from α nitration) could be detected by nmr for the mononitrated products. 1-Nitrotriptycene has a peak for one bridgehead proton at τ 3.4 (unspecified solvent),¹⁰ and a small peak was detected at 3.45 (CDCl₃) or 3.49 (DMSO-*d*₆) in one fraction of the nitration mixture.

Focusing attention first on the specificity of β nitration, we can make the following remarks: specific β nitration is in accord with previous observations; the acetylation of triptycene leads to a very high yield of 2-acetyltriptycene;¹⁰ β nitration is found for the nitration of 9,10-dihydro-9,10-ethanoanthracene

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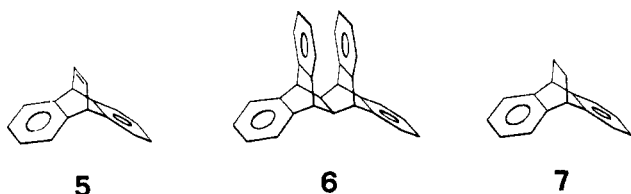
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TABLE I
 NITRATION OF TRIPTYCENE

N/1	t, hr	1 ^a	2 ^a	3 + 4 ^c	k ₁ ^b l./mol hr	k ₂ ^b l./mol hr	k ₁ ^c hr ⁻¹	k ₁ /k ₂	
1.84	1	17.0 (16.2)	68.0 (67.9)	15.0 (15.9)	21.5	3.87	0.594	5.6	
	2	14.9 (14.7)	68.6 (71.0)	16.5 (14.3)	16.7	2.95		5.7	
	3	13.7 (13.9)	68.8 (68.8)	17.5 (17.3)	15.9	2.80		5.7	
	4	12.9 (12.9)	68.8 (67.2)	18.3 (19.9)	16.1	2.82		5.7	
	6	11.8 (12.5)	68.9 (68.1)	19.3 (19.4)	16.9	2.95		5.7	
	30	(6.2)	(69.1)	(24.7)	25.7	3.99		6.4	
								Average	5.8
1.38	1	26.0 (25.0)	65.1 (64.3)	8.9 (10.7)	23.9	3.84	0.594	6.2	
	2	23.9 (24.3)	66.2 (67.1)	9.9 (8.6)	19.0	3.04		6.3	
	3	21.9 (21.9)	67.2 (66.9)	10.9 (11.2)	19.4	3.13		6.2	
	4	20.3 (20.0)	67.9 (69.1)	11.8 (10.9)	20.9	3.40		6.1	
	6	18.1 (18.4)	68.9 (67.6)	13.0 (14.0)	23.8	3.82		6.2	
	30	(13.1)	(72.6)	(14.3)	33.8	4.42		7.6	
								Average	6.4
0.92	1	54.9 (54.9)	42.3 (42.3)	2.8 (2.8)	13.7	2.52	0.594	5.4	
	2	47.5 (47.5)	47.5 (47.5)	5.0 (5.0)	14.5	3.38		4.3	
	3	42.9 (42.7)	50.7 (50.6)	6.4 (6.7)	18.0	4.33		4.2	
	4	40.2 (42.9)	52.6 (53.1)	7.2 (4.0)	22.0	5.35		4.1	
	6	36.8 (36.8)	55.0 (55.0)	8.2 (8.2)	29.1	6.89		4.2	
	30	(27.8)	(64.1)	(8.1)	64.0	9.7		6.6	
								Average	4.8
								Grand average	5.7

^a The first figures represent the smoothed results obtained from plotting the raw figures (in parentheses) obtained from the nmr analyses. ^b Values k_1 and k_2 are second-order rate constants. The most consistent values for k_1 and k_2 were obtained by using N as first order rather than second order. The ratio of k_1/k_2 was constant, regardless of the order used for N. ^c Value k_3 is a first-order rate constant which incorporates solvent concentration.

(5);¹¹ predominant β nitration (13:1) has been observed for janusene (6);¹² and 9,10-dihydro-9,10-ethanoanthracene (7) has been shown to undergo predom-



inantly β nitration, not only for mononitration, but also for further nitrations, such that ultimately 2,3,6,7-tetranitro-9,10-dihydro-9,10-ethanoanthracene could be obtained.¹³ The observed β nitration may be ascribed to resonance effects, steric factors, and/or strained-ring effects. Transannular resonance-type effects need not be invoked on the basis that predominant β nitration has been observed for benzobicyclo[2.2.1]heptene (8) and benzobicyclo[2.2.2]octene (9) in 13.5:1 and



29.3:1 ratios for β : α nitration, respectively.^{14,15} Because random nitration occurs for the corresponding nonbridged systems, indan and tetralin, and relatively

more β nitration is observed for 9, which has a bulkier bridge, steric effects described as the "fused *ortho* effect"^{14,15} are undoubtedly important in the systems under discussion. However, Streitwieser and coworkers have recently shown by protodetritiation and tritioderprotonation experiments with biphenylene and triptycene that "aryl positions adjacent to a fused strained ring have enhanced acidity and reduced reactivity toward electrophilic substitution."¹⁶ Strained-ring effects cannot be the only factor operating in β nitration because of the greater specificity observed for 9 vs. 8, which has a less bulky bridge and more strain. Moreover, we obtain a β : α nitration ratio of ca. 40:1 in the nitration of triptycene, in contrast to a predicted ratio of 7.8:1 on the basis of strained-ring effects alone.¹⁶ (For biphenylene, strained-ring effects cannot account for the specific orientation observed in dinitration and diacetylation,¹⁷ and thus strained-ring and resonance effects are occurring simultaneously in this system.) Therefore, specific β nitration in bridged systems can be explained by a combination of steric and strained-ring effects. Further data, such as kinetic studies and competitive nitrations with standard systems, must be drawn upon to clarify the possible operation of transannular resonance effects in systems where this possibility exists.

To determine the relative nitration rates for triptycene and 2-nitrotriptycene, a kinetic study was undertaken. Nitration reactions were checked at various time intervals by quenching aliquots in water and analyzing the worked-up fractions by nmr. The relative ratios of products were then graphed and the

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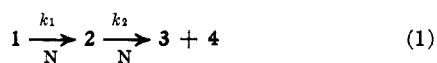
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smoothed points were analyzed by an analog computer set up on the basis of eq 1-5 where (N) = (nitrating



$$-\frac{d1}{dt} = k_1(1)(N) \quad (2)$$

$$\frac{d2}{dt} = k_1(1)(N) - k_2(2)(N) \quad (3)$$

$$\frac{d(3 + 4)}{dt} = k_2(2)(N) \quad (4)$$

$$-\frac{dN}{dt} = k_1(1)(N) + k_2(2)(N) + k_3(N) \quad (5)$$

species) \approx (HNO₃), and $k_3(N)$ accounts for the reaction of N with solvent.¹⁸ Table I shows the results obtained for the three concentrations of nitric acid used. The average k_1/k_2 value of 5.7 compares fairly well with our value of 9 obtained from an independent set of competitive nitrations of triptycene and 2-nitrotriptycene with 9,10-dihydro-9,10-ethanoanthracene.

Correcting a k_1/k_2 value of 7.4 (average of 5.7 and 9) for statistical effects gives 4.8. (A mononitrated triptycene has only two rings available for further nitration on a competitive basis with the three rings of triptycene.) If an analogy is now made by using the Hammett equation, $\log(k_2/k_1) = \rho(\sigma_1 + \sigma_2)$, where k_1 = rate of nitration of triptycene and k_2 = rate of nitration of a substituted triptycene, 2-nitrotriptycene, $\sigma_2 = 0.80/2.8$, the value¹⁹ for the polar substituent constant for NO₂ divided by the factor of 2.8 for the reduction of the inductive effect by the interposition of the methine groups of the triptycene system,²⁰ and $\sigma_1 = 0.49/5$, the value¹⁹ for the polar substituent constant for H divided by a factor of 5 to compensate for the methine groups,²⁰ then solving for ρ gives a value of -1.8 . By way of comparison, a ρ value of -7.22 is obtained for the nitration of mono-substituted benzenes by nitric acid in acetic anhydride at 25°²¹ where resonance effects are operative.²²⁻²⁴

Having obtained a measure of general electronic effects exerted in the triptycene system, we can now proceed to clarify which type of electronic effect may be predominating. Three types of electronic effects should be considered: transannular resonance, transannular polarization (or field effect), and inductive effects. Most significant is the fact that 9,10-dihydro-9,10-ethanoanthracene is nitrated 1.7 times as fast as triptycene (2.6 times as fast per ring). Therefore, whatever effect is operating in triptycene is electron withdrawing, and transannular resonance effects are

ruled out or at best very small. The formation of approximately equal amounts of dinitrotriptycenes further tends to rule out any significant resonance effects. Transannular polarization effects can also be ruled out because nitration studies of janusene show that a transannular polarization effect enhances nitration even for a ring which is affected by a nitrated aromatic ring.¹² Consequently, the predominant electronic effect operating in the triptycene system is the inductive effect, and the ρ value of -1.8 for the nitration gives a measure of the magnitude of this effect. It is noteworthy that mononitration of 9,10-dihydro-9,10-ethanoanthracene leads to convenient preparation of the β -mononitro product without complication from dinitro products. The added aromatic ring in triptycene adds enough unfavorable inductive effect to prevent ready preparation of 2-nitrotriptycene without contamination from the dinitro products.

Recently, the nitration of 9,10-dimethyltriptycene has been reported.²⁵ A 37% yield of 2-nitro-9,10-dimethyltriptycene was obtained *via* chromatographic techniques from a nitration reaction carried out in a manner somewhat similar to our procedure. No dinitrated products were reported; however, they were most likely formed inasmuch as we characterized dinitrated products in addition to a 38% yield of 2-nitrotriptycene from a corresponding nitration of triptycene.

Experimental Section²⁶

Product Studies.—To a solution of 12.6 g (0.050 mol) of 1 in 300 ml of acetic anhydride at 27° was added a solution of 6.0 ml of concentrated nitric acid in 10 ml of glacial acetic acid, the temperature being maintained at 27–29°. After 3 hr the reaction mixture was added to 800 ml of water. The precipitate which formed upon standing was removed by filtration, suspended in 50 ml of methylene chloride, chromatographed on a Florisil column packed in petroleum ether (bp 35–60°), and eluted with 10:90 methylene chloride–petroleum ether. The first fractions contained 1 and 2 (1.9 g); the second fractions represented 6.5 g, mp 268–271°, of pure 2 (lit.¹⁰ mp 269–270°); and 4.2 g of final fractions were recrystallized from ethyl acetate to give 1.3 g of 3, mp >350°.

Anal. Calcd for C₂₀H₁₂N₂O₄: C, 69.8; H, 3.5; N, 8.1. Found: C, 69.6; H, 3.3; N, 8.4.

The nmr spectrum (DMSO-*d*₆) shows aromatic proton absorption at τ 1.6–3.0 and a singlet at 3.82. (Compound 4 would require two closely spaced singlets for the bridgehead protons, and reaction mixtures did show two such singlets, chemical shift = 5 Hz, centered around τ 3.82. Comparison of bridgehead proton areas indicated that 3 and 4 were formed in comparable amounts.)

In a similar experiment, the precipitate (15 g), which formed when the reaction mixture was added to water, was treated with a mixture of methylene chloride and benzene. This solution was filtered to remove 210 mg of relatively insoluble material, dried with sodium sulfate, and concentrated to a small volume. The precipitate (11.4 g) which formed upon cooling was removed by filtration, and an aliquot of the filtrate, containing 2.5 g of solids, was analyzed by nmr. In addition to bridgehead proton absorption for 1, 2, 3, and 4, the nmr spectrum (DMSO-*d*₆) showed a peak at τ 3.49 with an area equal to 10% of the total bridgehead proton absorption. An nmr analysis of the original reaction precipitate indicated the formation of 72% mononitrated products, and therefore the material with bridgehead absorption at τ 3.49 represents 2.3% mononitrated products, assuming that

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(26) Nmr spectra were determined with a Varian A-60 spectrophotometer using tetramethylsilane as an internal reference and vpc analyses were obtained with a F & M (Hewlett Packard) Model 720 dual-column programmed-temperature gas chromatograph.

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(22) A similar two-point plot can be made from the relative rates of nitration of 9,10-dihydro-9,10-ethanoanthracene and triptycene. By using polar substituent constant values for ethyl and benzyl,¹⁹ a ρ value of -2.0 is obtained. The similarity of the resulting ρ values may be coincidental because of the various assumptions involved in these calculations.

(23) The nitration of diphenylmethane cannot be used as a model reaction because of various types of reactions that occur with the methylene group. See A. I. Titov, *Zh. Obshch. Khim.*, **18**, 1312 (1948) [*Chem. Abstr.*, **43**, 4217a (1949)], and M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 3079 (1958).

(24) The value range of 7–10 for the ratio of $F_{\beta}L'\beta$ - to $F_{\beta}L\beta$ -dinitrojanusene formed in the nitration of F_{β} -nitrojanusene¹³ is in accord with our values for k_1/k_2 . The nitration of the L' and L rings of F_{β} -nitrojanusene serves as a good model for the nitrations of triptycene and 2-nitrotriptycene.

all of this material was concentrated into the last fraction containing the more soluble components. (The τ 3.49 peak was not observed in the nmr spectrum of the original reaction precipitate.)

Kinetic Studies.—Each reaction mixture was carried out in a constant-temperature water bath at $29 \pm 1^\circ$. To solutions of 12.7 g (0.050 mol) of 1 in 500 ml of acetic anhydride at 29° were added the respective amounts [6.0 ml (0.092 mol), 4.5 ml (0.069 mol), or 3.0 ml (0.046 mol)] of concentrated nitric acid (68%) in 7.5 ml of glacial acetic acid. Periodically, 5-ml aliquots were removed and added to 25-ml portions of water. Each sample was shaken for 4 min until the acetic anhydride was decomposed. The solids from each sample were removed by filtration and washed with water. The entire precipitate in each case was analyzed by nmr. The nmr analyses (DMSO- d_6) were carried out by relative integration of the bridgehead proton areas at τ 4.34 for 1, 4.05 and 4.10 for 2, and 3.78, 3.82, and 3.86 for 3 and 4.

Competitive Nitrations. 9,10-Dihydro-9,10-ethanoanthracene (7) vs. Triptycene (1).—A mixture of 516 mg (0.0025 mol) of 7, 636 mg (0.0025 mol) of 1, and 565 mg of eicosane (internal standard) was dissolved in a small amount of methylene chloride, and an aliquot was removed for vpc analysis. After removal of the solvent, 25 ml of nitromethane and 25 ml of acetic anhydride were added, and the reaction mixture was placed in a 29° constant-temperature bath. Upon addition of 0.16 ml (0.0025 mol) of concentrated nitric acid (68%), the reaction was allowed to

proceed for 5 hr at 29° before the product was added to water, which hydrolyzed the acetic anhydride. The mixture was extracted with methylene chloride, and the resulting solution was dried with sodium sulfate and concentrated to a small volume for vpc analysis. The vpc analyses were carried out on a 4-ft 10% silicone rubber SE-52 column at 250° . The results showed 53% of 7 and 69% of 1 remaining at the end of the reaction. By using the expression, $\log([A]/[A_0])/\log([B]/[B_0]) = k_A/k_B$, where [A] and [B] refer to final concentrations of 7 and 1, respectively, and where $[A_0]$ and $[B_0]$ refer to initial concentrations; $k_7/k_1 \cong 1.7$.

9,10-Dihydro-9,10-ethanoanthracene (7) vs. 2-Nitrotriptycene (2).—An experiment similar to the one above was carried out with 258 mg (0.00125 mol) of 7, 374 mg (0.00125 mol) of 2, 300 mg of eicosane, 0.16 ml (0.0025 mol) of concentrated nitric acid, 25 ml of nitromethane, and 25 ml of acetic anhydride. The results of the vpc analyses (240° , programmed at $10^\circ/\text{min}$ to hold at 300°) showed 28% of 7 and 92.5% of 2 remaining at the end of the reaction, so that $k_7/k_2 \cong 16$ and $k_1/k_2 \cong 9$.

Registry No.—1, 477-75-8; 3, 18339-75-8.

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Reactions of Acyl Isocyanates

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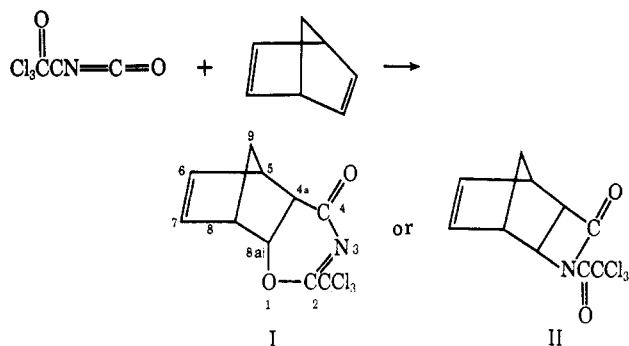
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The reaction of norbornadiene with trichloroacetyl isocyanate is shown to proceed *via* a novel cyclization to give tetrahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxan-4-one. The structure of this product and the mechanism of its formation is discussed. Similar reactions occurred with norbornene and dicyclopentadiene. Enamines and vinyl ethers reacted with acyl isocyanates to give adducts in which the isocyanate had, in effect, replaced the β proton of the enamine or vinyl ether. Adducts of acyl isocyanates with indole and pyrrole are reported. Reactions of N,N-disubstituted formamides with trichloroacetyl isocyanate proceeded with the loss of carbon dioxide and formation of acyl formamidines. Conventional reactions of acyl isocyanates with nucleophiles are reported.

The discovery of a facile preparative route to acyl isocyanates from the reaction of amides with oxalyl chloride¹ prompted us to investigate their reactions. Of particular interest were reactions involving the unique diene $[-(C=O)N=C<]$ and dienophile $(-N=C<)$ systems present in acyl isocyanates.

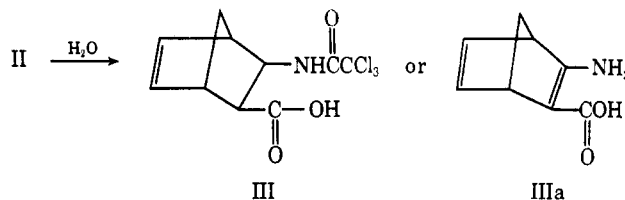
The electron-deficient dienophiles, maleic anhydride and dimethyl acetylenedicarboxylate, did not react with trichloroacetyl isocyanate. The nucleophilic olefin norbornadiene, however, gave a 1:1 adduct I,



mp $83\text{--}85^\circ$. Hydrolysis and spectral data indicate that the adduct is 4a,5,8,8a-tetrahydro-2-trichloromethyl-5,8-methano-4H-1,3-benzoxazin-4-one (I) rather than the alternate structure II or some product involving molecular rearrangement.

The infrared absorptions of the adduct at 1706 and 1603 cm^{-1} are quite consistent for the $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups in I. These values are not consistent for II, a fused β -lactam, which have been shown² to absorb at 1770 to 1789 cm^{-1} . The nmr spectrum of the adduct, along with tentative peak assignments and the spectra of related derivatives, is reported in Table I.

The hydrolysis of II should lead to the carboxylic acid III or IIIa assuming that a β -lactam would hydrolyze faster than a trichloroacetamide. Con-



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