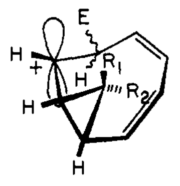
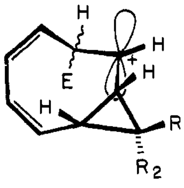


10

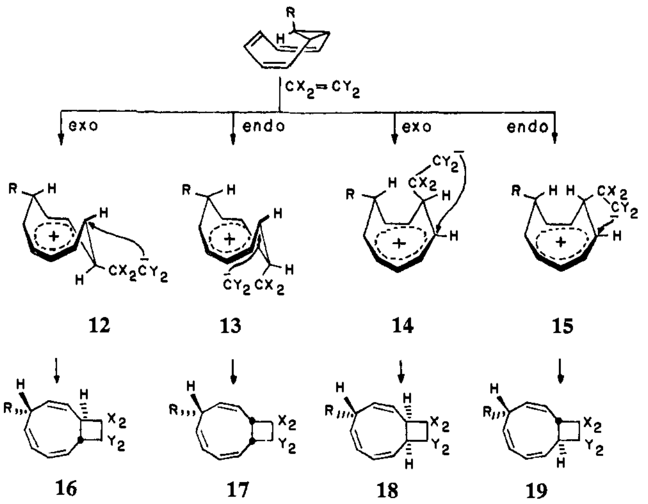


11

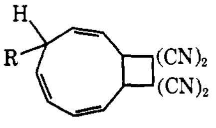
countering destabilization of the cationic center.[11] In this frame of reference, then, **8a**, **8b**, and other syn 9-substituted derivatives of **1** are expected to react slowly, if at all, in the midst of discriminating electrophiles.

Addition as depicted in **10** can ultimately lead with a small readjustment of bond angles to 1,3-bishomotropylium ion intermediates. In view of the established "aromatic" nature of these entities,[3] a driving force in this direction is certainly present. The results with **6** are now convincingly and perhaps uniquely accommodated by that pathway from among the four mechanistic options (Scheme I) in which exo bonding of CSI to C_3 occurs initially, perhaps for steric reasons. The stereochemical features of **7** necessitate further that this interesting cationic intermediate possess trans-disposed methylene bridges as in **12**.[12] Collapse of this zwitterion with C–N bond formation leads ultimately to trans-fused heterobicyclo[7.2.0]undecatriene **16**.

Scheme I



Such reactions appear to be entirely general. For example, tetracyanoethylene condenses with **1** and **6** in tetrahydrofuran solution at *ambient temperature*[6] to furnish uniquely the adducts **20a**, mp 140.5–141°, $\lambda_{max}^{C_2H_5OH}$ 225 nm (ϵ 7250),[4] and **20b**, mp 152–153°,[6] $\lambda_{max}^{C_2H_5OH}$ 231 nm (ϵ 11,240), respectively. Trienes **8a** and **8b** are again unreactive to this reagent under the conditions employed. In keeping with the mechanistic scheme outlined herein, both **20a** and **20b** should be trans fused and not of cis stereochemistry.[2b] X-Ray crystal-structure analyses of these substances are in progress.



20a, R = H
b, R = CH_3

Acknowledgment. The authors at The Ohio State University thank the National Science Foundation and Eli Lilly and Company for financial assistance. The authors at Iowa State University thank the Ames Laboratory of the U. S. Atomic Energy Commission for support.

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[11] (a) J. C. Martin and B. R. Ree, *J. Amer. Chem. Soc.*, **91**, 5882 (1969); **92**, 1660 (1970); (b) P. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1960); V. Buss, R. Gleiter, and P. von R. Schleyer, *ibid.*, **93**, 3927 (1971).

[12] Warner and Winstein[3] have examined the protonation of 1 and have concluded that the resulting 1,3-bishomotropylium ion is cis disposed. It remains to determine if the same cations are involved in the two studies (work in progress).

[13] Holder of a NATO Postdoctoral Fellowship (1970–1972) administered by the Science Research Council.

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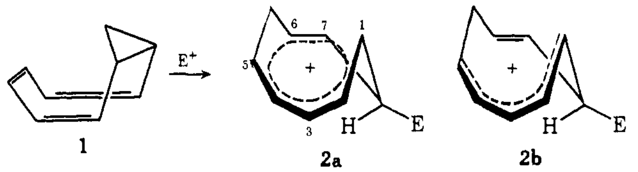
Substituent Effects on the Nonconcerted Cycloaddition of Chlorosulfonyl Isocyanate to *cis*-Bicyclo[6.1.0]nonatriene Derivatives[1]

Sir:

Available experimental evidence indicates that *cis*-bicyclo[6.1.0]nonatriene (**1**) and its anti 9-substituted derivatives undergo impressively stereocontrolled electrophilic additions.[2] As noted in the preceding paper,[2] electrophilic attack at C_3 of the syn conformer of **1** should be kinetically favored, for this process uniquely gives rise to a delocalized cation **2a** which initially must necessarily have a trans orientation. However, because **2a** is a double Möbius bishomotropylium ion, the 6,7 double bond requires significant twisting to achieve satisfactory overlap. As a result, the question of actual charge delocalization in **2a** gains significance and the possible alternative involvement of the noninteracting structure **2b** with a simple pentadienyl unit and an isolated double bond must be considered. In an effort to understand more completely the factors which govern the intriguing reactivity of such polyenes, we have examined the cycloaddition of chlorosulfonyl isocyanate (CSI) to several derivatives of **1** bearing substituents on the medium ring.



1 **2a** **2b**

Addition of dichloromethane to a liquid ammonia solution of methylcyclooctatetraenyl dianion proceeded to give all four possible methyl-*cis*-bicyclo[6.1.0]-nonatrienes (**3**–**6**). These were separated and purified by preparative scale vpc (15% PPGA on Chromosorb P at 65°) and assigned individual structures on the basis

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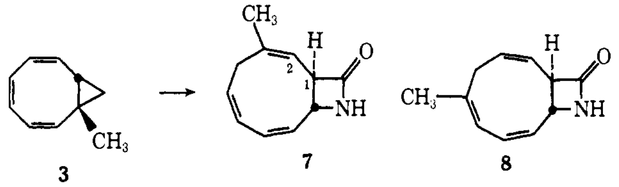
[1] Unsaturated Heterocyclic Systems. LXXXVII. The preceding paper in this series is given in ref 2.

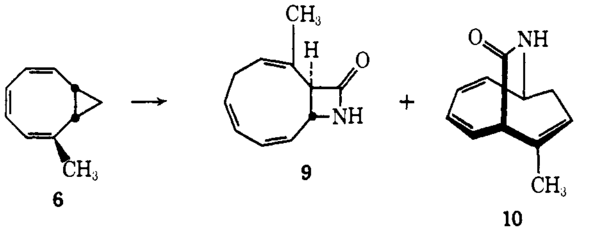
[2] L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 630 (1972).

of chemical conversions to compounds of known structure.[3,4] Exposure of **3** to 1 equiv of CSI in refluxing dichloromethane and subsequent dechlorosulfonylation gave rise in 53% yield to a homogeneous white solid, mp 145.5–146.5°,[3] $\lambda_{max}^{C_2H_5OH}$ 225 nm (ϵ 3600), formulated as **7** chiefly on the basis of double and triple resonance studies at 100 MHz. No evidence was gained for the formation of other products such as β-lactam **8**.



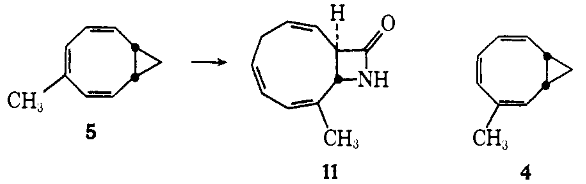
3 **7** **8**

Similar treatment of **6** resulted in the isolation of two lactams. The major product (mp 145.5–146°,[3] 53.5% yield) showed an infrared carbonyl band at 1760 cm^{-1} as well as electronic [$\lambda_{max}^{C_2H_5OH}$ 224 nm (ϵ 4140)] and 60-MHz nmr spectra compatible with structure **9**. Further confirmation of this assignment was provided by spin decoupling measurements. The minor adduct (mp 135.5–137.5°,[3] 5% yield) was clearly not a β-lactam ($\nu_{max}^{CHCl_3}$ 1660 cm^{-1}). Findings derived from double and triple irradiation experiments, coupled with the ultraviolet datum [$\lambda_{max}^{C_2H_5OH}$ 215 sh (ϵ 4250) and 254 nm (3560)] support structure **10** for this substance.



6 **9** **10**

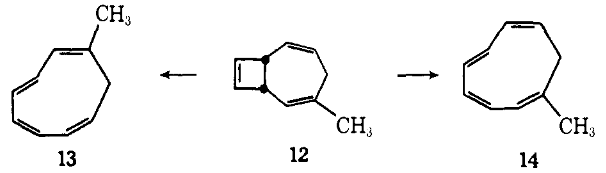
Like reaction of **5** with CSI, but for much shortened reaction times, gave a single β-lactam [**11**, mp 123.5–124°,[3] $\lambda_{max}^{C_2H_5OH}$ 228 nm (ϵ 4670)] albeit in low (6%) yield. These conditions were resorted to when infrared-monitored reactions revealed that although the *N*-chlorosulfonyl β-lactam carbonyl band (1825 cm^{-1}) developed as expected, it also decayed at an appreciable rate prior to the time of total CSI consumption in favor of a broad ill-defined absorption at 1750 cm^{-1}. To all appearances, the nonkinetically controlled product was polymeric in nature. The nmr spectrum of **1b** consists, *inter alia*, of peaks attributable to >C*H*CO- and >C*H*-N<, the latter appearing as a narrow doublet (|*J*| = 2.5 Hz).



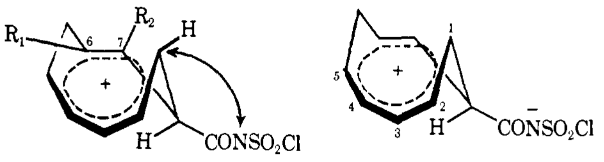
5 **11** **4**

In the case of **4**, it was not possible to bypass polymer formation in a satisfactory way; accordingly, β-lactams were not isolated. Competitive reaction studies with **3**–**6** revealed, however, that **4** reacts no faster with CSI than its isomers; in fact, our results suggest a reactivity order of **5** > **3** > **4** ~ **6**. No pronounced kinetic inequalities were seen, the spread in reactivity being only a factor of <2 (1.7:1.3:1.0:1.0, respectively).

The exclusive formation of **7** from **3** (and of **9** from **6**) once again is not compatible with the intervention of 1,3,5,7-*cis*^{2},*trans*,*cis*-cyclononatetraene intermediates since, for example, unidirectional conrotatory ring opening of **12** (the 3,3-sigmatropic rearrangement product of **3**)[5,6] only to **13** does not appear reasonable. Rather, the selective formation of these β-lactams can be viewed as the result of electrophilic attack at C$_3$ with intermediate generation of *trans*-1,3-bishomotropylium ions **15a** and **15b**, respectively. The absence of other adducts (*e.g.*, **8**) among the reaction products cannot be construed as discounting electrophilic attack at C$_6$ in either **3** or **6**. Rather, when proper attention is given to the structural features of the *trans*-1,3-bishomotropylium ions (**16a** and **16b**, respectively) anticipated from such reactions, it is seen that these two intermediates share the common parameter of methyl substitution on the pentadienyl segment of the cation. In contrast, the methyl groups in ions **15a** and **15b** are bonded to the ethylene segment. Since the positive charge in such ions is recognized to be localized most heavily on the pentadienyl carbon segment,[7] the methyl groups in **16a** and **16b** will be required to interact hyperconjugatively with the adjacent ring carbons to a substantially greater extent than those in **15a** and **15b**. Consequently, proton loss from the methyl groups in **16a** and **16b** is very likely to become competitive with cyclization (the latter process is apparently reversible, at least in certain instances), with the result that the substituted polyene so formed undergoes polymerization.



13 **12** **14**



15a, R$_1$ = CH$_3$; R$_2$ = H
b, R$_1$ = H; R$_2$ = CH$_3$

16a, CH$_3$ at C$_5$
b, CH$_3$ at C$_4$
c, CH$_3$ at C$_3$
d, CH$_3$ at C$_2$
e, CH$_3$ at C$_1$

The behavior of trienes **4** and **5** is likewise accommodated by this interpretation. In the particular case of **5**, the successful isolation of **11** after short reaction times is possible because of the more favorable positioning of the methyl group in **16d** relative to **16e**. Our inability to isolate a cycloadduct from **4** may follow then from the positioning of the methyl substituent in **16c**.[8] Although **10** may arise in one of several ways, its

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(3) Satisfactory elementary analyses were obtained for all new compounds.

(4) Full details of this work will appear in our full paper.

(5) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).

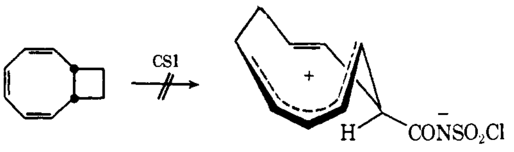
(6) L. A. Paquette and M. J. Epstein, *ibid.*, **93**, 5936 (1971).

(7) This point has been elegantly demonstrated by nmr studies on the 1,3-bishomotropylium generated by protonation of **1**: P. Warner and S. Winstein, *ibid.*, **93**, 1284 (1971).

(8) We presently leave open the question dealing with possible elctrophilic attack at the substituent-bearing carbon in **4**.

genesis is most satisfactorily rationalized in terms of the cis isomer of **15b**. The somewhat unique capability of **15b** to undergo detectable inversion of that methylene bridge which bears the $-CON^{-}SO_2Cl$ group would appear to be related to the enhanced ground-state strain of this ion which is engendered by the proximity of the methyl substituent.

The ring-methylated derivatives of **1** do behave as if the charge distribution in the intermediate zwitterions is that expected for **2b**; however, complicating factors (polymer formation) do exist. As a result, an accurate assessment of the extent of positive charge borne by C_6 and C_7 in the *trans*-1,3-bishomotropylium ions cannot be made at this time. The overriding energy factor is undoubtedly maximal charge localization on the longest linearly conjugated carbon segment; but "aromaticity," if inherent in such a structural type, necessitates the development of a certain amount of ring current. Further comments on this point are not warranted until additional studies, presently in progress, are completed. It is interesting that *cis*-bicyclo[6.2.0]deca-2,4,6-triene (**17**) whose interaction with CSI might be expected to lead to pentadienyl cation **18** does not react with this electrophile (CH_2Cl_2, reflux 100 hr, 94.5% recovery). The failure of this cycloaddition may, however, be conformationally related.[2]



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Acknowledgment. We acknowledge with gratitude the financial support of the National Science Foundation and Eli Lilly and Company.

(9) Holder of a NATO Postdoctoral Fellowship (1970–1972) administered by the Science Research Council.

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Photocyclization Mechanism of N-Substituted Diphenylamines

Sir:

The photocyclization of aromatic amines to carbazoles has been investigated by a number of authors.[1] In flash kinetic studies with *N*-methyldiphenylamine (A), Linschitz and Grellmann have found a transient with an absorption maximum at 610 nm.[2] They proposed that this 610 transient is the 11,12-dihydrocarbazole[3] which is formed *via* the amine triplet and which reacts further either to the carbazole or back to the amine (eq 1–6). This mechanism has been questioned

$$^3A^* \xrightarrow{k_1} 610 \tag{1}$$

$$^3A^* + M \xrightarrow{k_2} {}^1A + M \tag{2}$$

$$^3A^* + O_2 \xrightarrow{k_3} {}^1A + O_2 \tag{3}$$

$$610 \xrightarrow{k_4} \text{carbazole} + H_2 \tag{4}$$

$$610 + O_2 \xrightarrow{k_5} \text{carbazole} + H_2O_2 \tag{5}$$

$$610 \xrightarrow{k_6} {}^1A \tag{6}$$

recently.[5] We wish to present experimental results from flash photolytic studies which prove it to be correct. The apparatus used has been described elsewhere.[6]

In order to find out whether carbazole is indeed formed *via* 610 (step 4 or 5) we compared flash decay curves at 341 and 610 nm in degassed with those in aerated solutions.[7] At both wavelengths the amine does not absorb, at 341 nm both the carbazole and the transient absorb, and at 610 nm only the transient absorbs.

In the aerated solution the optical density at 341 nm changes irreversibly within the lifetime of the flash (Figure 1d). There are two explanations for this observation. (a) Carbazole is formed within the lifetime of the flash, *i.e.*, much faster than 610 decays. (b) The 610 decay and the carbazol growing in curves mutually compensate each other, because carbazole is formed *via* 610.

In a degassed solution, where there is practically no carbazole formation at room temperature ($k_4/k_6 \approx 10^{-2}$) the decay rate at 341 nm is exactly the same as at 610 nm (*cf.* Figure 1a and b). The ratio of the optical densities at zero time E_0^{610}/E_0^{341} (computed from the extrapolated curves in Figure 1, zero time being taken as the end of the flash excitation) has the same value in the aerated and in the degassed solution. Therefore the absorption in Figure 1d is, at zero time, entirely due to the 610 and, at infinite time, entirely due to carbazole absorption, which means explanation b is the correct one.

At low temperatures in degassed solutions, where (in contrast to room temperature) appreciable amounts of carbazole are formed ($k_4/k_6 \gg 1$), the transient absorptions at 341 and 610 nm show the same behavior as in the aerated solution, because the 610 transient is again the precursor of carbazole.

Steady state illumination experiments with propiophenone as sensitizer[8] already indicated that the formation of carbazole proceeds *via* the triplet state of the amine. In flash experiments at room temperature with a degassed solution containing 10^{-3} *M* *N*-methyldiphenylamine and 10^{-2} *M* propionphenone in methylcyclohexane, under conditions where only the propiophenone was excited, we could observe the 610 transient absorption. The direct formation (without sensitizer)

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(1) (a) C. A. Parker and N. J. Barnes, *Analyst (London)*, **82**, 606 (1957); (b) E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 202 (1963); (c) G. C. Terry, V. E. Uffindell, and F. W. Willets, *Nature (London)*, **223**, 1050 (1969).

(2) K. H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1881 (1963); H. Linschitz and K. H. Grellmann, *ibid.*, **86**, 303 (1964).

(3) In a pulse radiolytic study of triphenylamine,[4] Kemp, *et al.*, assigned the 610 transient erroneously to the amine triplet.

(4) T. I. Kemp, J. P. Robert, G. A. Salmon, and G. F. Thompson, *J. Phys. Chem.*, 71, 3052 (1967); 72, 1464 (1968).

(5) H. Shizuka, Y. Takayama, J. Tanaka, and T. Morita, *J. Amer. Chem. Soc.*, **92**, 7270 (1970); see also ref 1c.

(6) K. H. Grellmann, E. Heilbronner, P. Seiler, and A. Weller, *ibid.*, **90**, 4238 (1968).

(7) There is no wavelength detectable at which the photoproduct carbazole absorbs significantly stronger than the 610 transient. For this reason no "growing in curve" such as in Figure 2b can be observed.

(8) E. Tauer, M.S. Thesis, University Erlangen, Germany, 1966; see also ref 5.