lower enthalpy because its methyl group is adjacent to a =CH rather than to a purely σ-bonded >CH₂ group. For the ethylcyclopentenes the difference in nonbonded interactions of the two isomers increases,

and the equilibrium is farther shifted toward the 3-ethyl isomer (part I of this series, Table I).[1]

# Cycloadditions. III. Reactions of Δ²-1,2,3-Triazolines with Phenyl Isocyanate and Phenyl Isothiocyanate[1]

John E. Baldwin, Gary V. Kaiser,[2] and Judith A. Romersberger[2]

Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803. Received May 22, 1965

The cyclopentene–phenyl azide adduct and phenyl isothiocyanate react at 110° to give nitrogen and 2-anilinocyclopentenylthiocarbanilide. The norbornene–phenyl azide adduct and phenyl isocyanate react at 160° to give nitrogen and a 4,10-diphenyl-4,10-diazatricyclo-[4.2.1.1²,⁵]decan-3-one. These reactions, previously[3] thought to give symmetrical thioureas or ureas and interpreted as proceeding via 1,3-dipolar intermediates, are reconsidered mechanistically.

Introduction

According to the literature,[3] heating the Δ²-1,2,3-triazolines 1 or 4 with phenyl isothiocyanate or phenyl isocyanate leads in high yield to the symmetrical diphenylthiourea 3 or urea 6. These reactions are held[3] to proceed by thermal decomposition of a triazoline to nitrogen and a 1,3-dipolar intermediate (2 or 5), followed by a "1,3-dipolar cycloaddition."
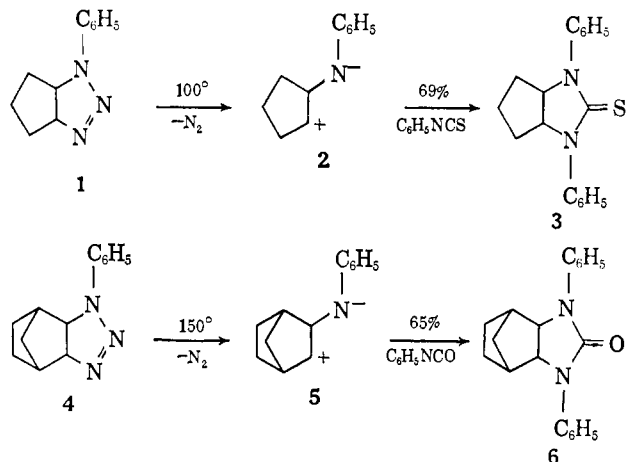

Among the several questions that these reactions and mechanistic conceptions raise, one concerned with the structures of the 1,3-dipolar intermediates 2 and 5

seemed of particular theoretical interest: should the dipolar forms 2 and 5 be taken literally, and/or might they permit product formation corresponding to both rearranged and unrearranged structures? The dipolar form 5 might be imagined particularly capable of leading to rearranged products, insofar as a bridged intermediate[4] such as 7 might be a more adequate representation for the posited intermediate.
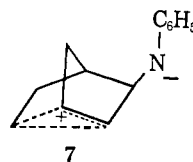
A reinvestigation of these reactions was initiated and has produced surprising results: the two reactions give dissimilar products and neither product is a urea. This paper presents evidence for new structural assignments for the products previously reported[3] as 3 and 6, and attempts to delineate their mechanistic significance.

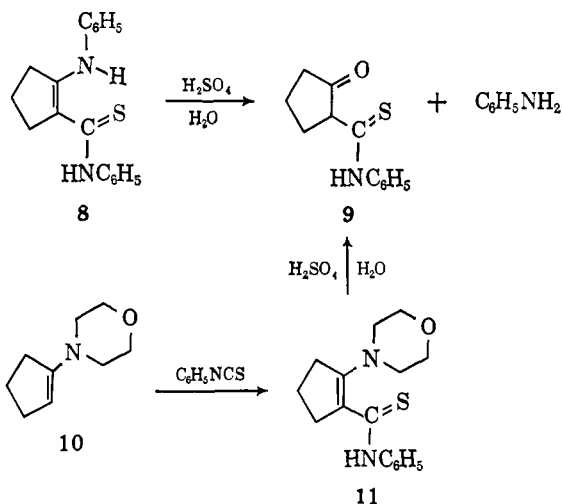## 2-Anilinocyclopentenylthiocarbanilide

When the cyclopentene–phenyl azide adduct, 4-phenyl-2,3,4-triazabicyclo[3.3.0]oct-2-ene (1), was heated with an excess of phenyl isothiocyanate in chlorobenzene at 110°, a 78% yield of product $C_{18}H_{18}N_2S$, m.p. 128.5–130.5°, was obtained. That this product, corresponding in molecular formula to an adduct of 2 and phenyl isothiocyanate, could not be formulated as the thiourea 3 was abundantly clear: the product is bright yellow and has $\lambda_{max}^{CHCl_3}$ at 386 mμ (ε 24,000) and 314 mμ (ε 9000) in the ultraviolet; its infrared spectrum shows $\nu_{max}^{CHCl_3}$ at 3390, 1612, 1595, 1580, 1500, 1390, and 1250 cm.⁻¹; and the n.m.r. spectrum of the product has absorptions at τ −3.0 (1 H), 2.0–3.4 (11 H), a multiplet centered at 7.25 (4 H), and a multiplet centered at 8.15 (2 H).

These spectral data were taken as evidence for a 1,2-disubstituted cyclopentene (four allylic protons at τ 7.25, two nonallylic methylene protons at 8.15) in which the double bond is conjugated with a thio-

(1) (a) Supported in part by the Petroleum Research Fund, administered by the American Chemical Society. (b) Cycloadditions. I: J. E. Baldwin, G. V. Kaiser, and J. A. Romersberger, *J. Am. Chem. Soc.*, 86, 4509 (1964); II: J. E. Baldwin, *Tetrahedron*, 20, 2933 (1964).
(2) National Science Foundation Undergraduate Research Participant.
(3) (a) R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, 2, 565 (1963); 2, 633 (1963), and references cited therein; (b) R. Huisgen, "Theoretische Chemie und Organische Synthesen," Festschrift der Zehnjahresfeier des Fonds der Chemischen Industrie, Düsseldorf, 1960.

(4) For a recent summary and analysis of carbonium ion rearrangements in bridged bicyclic systems, see J. A. Berson in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

carbanilide group. Thus structure **8** was postulated. Hydrolysis of $C_{18}H_{18}N_2S$ (**8**) gave aniline and 2-oxo-cyclopentylthiocarbanilide (**9**), which was rigorously identified through comparisons with an authentic sample synthesized independently[5] (**10** → **11** → **9**).

8

9

+ $C_6H_5NH_2$

10

11

While the combination of spectral and chemical evidence supporting structure **8** for the adduct seems definitive, the importance of possible tautomerization between **8** and **12** cannot be prejudged and has not been investigated. With this minor reservation in mind, structure **8**, 2-anilinocyclopentenylthiocarbanilide, is assigned to the $C_{18}H_{18}N_2S$ product derived from the cyclopentene–phenyl azide adduct and phenyl isothiocyanate.


12
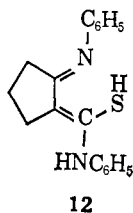
#### 4,10-Diphenyl-4,10-diazatricyclo[4.2.1.1^{2,5}]decan-2-one

When the norbornene–phenyl azide adduct, exo-3-phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene (**4**), was heated with an excess of phenyl isocyanate in o-di-chlorobenzene at 160°, there was obtained a 60% yield of product $C_{20}H_{20}N_2O$, m.p. 162–163° from cyclohexane. The n.m.r. spectrum of the adduct shows aromatic protons at τ 2.4–3.4 (10 H), a quartet at 4.7 (1 H), a quartet at 6.0 (1 H), a multiplet at 7.2–7.6 (2 H), and a complex absorption at 8.0–8.8 (6 H). The most striking feature of this n.m.r. spectrum is the quartets centered at τ 4.7 and 6.0, corresponding to one proton each. The two protons in the proposed[3] structure **6** which would be deshielded by adjacent nitrogen atoms in the molecule are equivalent, and could not give the observed spectrum. Thus structures **13** and **14** are rigorously excluded from further consideration as possible representations for the major isolable product.

The $C_{20}H_{20}N_2O$ product, having ν_{max}^{KBr} 1700 cm.$^{-1}$, was reduced by lithium aluminium hydride to an oil, $C_{20}H_{22}N_2$, free of any absorption bands in the carbonyl region. This evidence requires a carbonyl function in

(5) W. Reid and W. Käppeler, *Ann.*, **673**, 132 (1964).

13

14
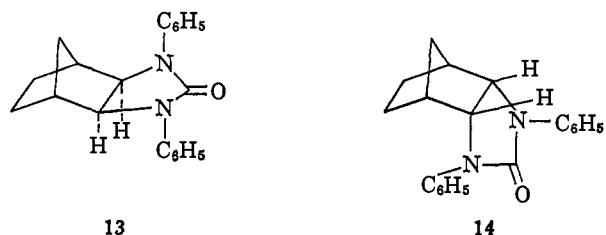
the adduct $C_{20}H_{20}N_2O$; several formal possibilities such as **15** and **16** derived from the dipolar form **5** and phenyl isocyanate by 1,3-cycloaddition across the carbon–oxygen double bond are thus eliminated as structural expressions for the adduct.

15

16
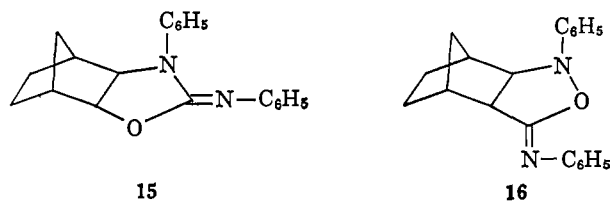
The $C_{20}H_{20}N_2O$ adduct was not reduced by hydrogen in the presence of platinum in glacial acetic acid. If this negative result is taken tentatively as prohibiting a carbon–carbon double bond in the molecule, the $C_{20}H_{20}N_2O$ adduct must have two phenyl groups, a carbonyl function, and three rings. Further, if the molecule lacks a carbon–carbon double bond, the proton at τ 4.7 in the n.m.r. cannot be vinylic and must be deshielded to this region by an appropriate combination of structural features.

Some of the more obvious structural candidates which have the required tricyclic skeleton, two non-equivalent deshielded hydrogens, and a carbonyl function are **17**, **18**, **19**, and **20**.

17

18

19

20
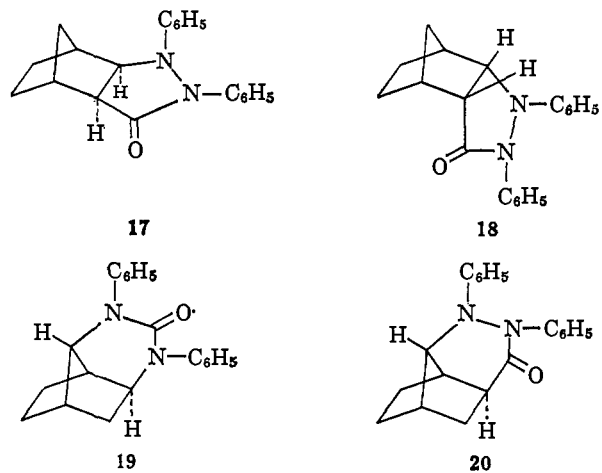
While it is possible to construct a fairly convincing case against these four candidates on the basis of discrepancies between anticipated and observed chemical shift parameters for the two deshielded protons in each structure, they may be debarred more quickly and conclusively through consideration of the results from spin–spin decoupling experiments.

The two quartets in the n.m.r. spectrum of the adduct at τ 4.7 and 6.0 (Figure 1a) result from spin–spin interactions of 2.3 c.p.s. between the two protons, 5.4 c.p.s. between the proton at τ 4.7 and one at 7.2, and 6.0 c.p.s. between the protons at τ 6.0 and 7.4. Irradi-
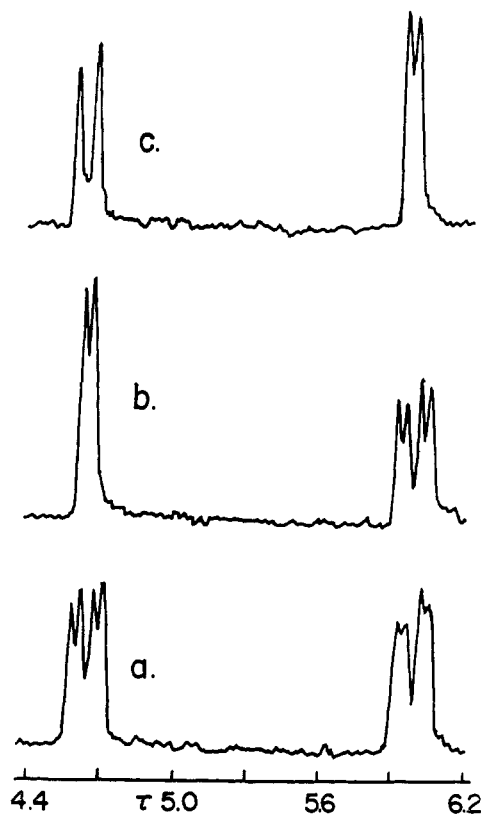
Figure 1. Double-resonance n.m.r. spectra of two deshielded protons in the $C_{20}H_{20}N_2O$ adduct: (a) $\omega_1 - \omega_2 = 0$, (b) $\omega_1 - \omega_2 = 150$ c.p.s., (c) $\omega_1 - \omega_2 = 82$ c.p.s.
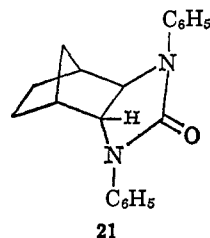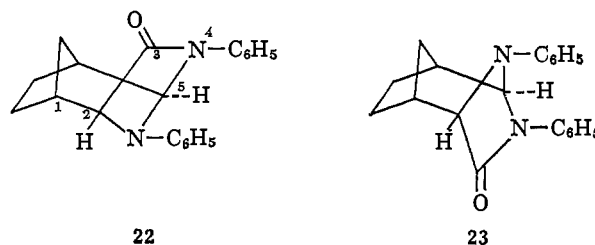

21

proton (3–6 c.p.s.), based on observed spin–spin interactions in less-strained norbornane derivatives, might not be pertinent.

We discard structure **21** on several grounds: examination of Dreiding models indicates that formation of **21** would involve a seemingly prohibitive amount of strain; we are aware of no precedent in the literature for a tricyclic skeletal structure of this type and stereochemistry; and structure **21** does not account for the ready protonation of the adduct (see below).

Thus it became clear that the $C_{20}H_{20}N_2O$ adduct must be derived from its formal constituents **5** and phenyl isocyanate through rearrangement at some stage or stages.

The structural proposal **22** for the adduct can accommodate all the available spectral and chemical data. Further reactions of the adduct are described in terms of this formulation.

22   **23**

ation in the region of τ 7.2 causes the quartet at τ 4.7 to collapse to a doublet with $J = 2.3$ c.p.s. (Figure 1b); irradiation in the region of τ 6.0 causes the same quartet to collapse to a doublet with $J = 5.4$ c.p.s. (Figure 1c); irradiation near τ 7.4 causes the quartet at τ 6.0 to collapse to a doublet with $J = 2.3$ c.p.s. (Figure 1c).

The spin–spin decoupling results are not compatible with structures **17, 18, 19,** or **20.** For **17** and **18** the expected[6] coupling constants for splitting between the two deshielded protons adjacent to carbonyl or nitrogen would be 5.8–7.7 and 8.9–11.4 c.p.s., respectively. These expectations are far removed from the observed value, 2.3 c.p.s. While a proton at the C-7 position of the norbornane system in **19** or **20** might be coupled to the other deshielded proton with J as large as 2.3 c.p.s., it would not[6] couple with any other proton in the structures **19** or **20** with a spin–spin interaction of 5.4 or 6.0 c.p.s., the observed values.

Another structure which has been suggested by others in informal discussions and should therefore be considered explicitly here is the *trans*-fused stereoisomer of **13, 21.**

This structure has the required tricyclic framework, carbonyl function, and nonequivalent deshielded hydrogens. Presumably it could be so strained that predictions[6] of the spin–spin coupling constants between the two deshielded protons (2.2–5.8 c.p.c.), between *exo*-proton and the adjacent bridgehead proton (*ca.* 0), and between *endo*-proton and its adjacent bridgehead

Structure **22**, in particular, provides an adequate basis for interpreting the n.m.r. spectral data. The proton at τ 4.7 could be assigned to the C-5 proton of **22,** strongly deshielded by two adjacent nitrogen functions, and that at 6.0 to the C-2 proton, deshielded by one adjacent nitrogen and by the carbonyl group. The "long-range" coupling between the two deshielded protons of 2.3 c.p.s. through four bonds is not extraordinary, for the four bonds are held in a fairly rigid planar configuration by the tricyclic skeleton, and such a planar disposition of bonds appears to facilitate long-range spin–spin coupling interactions.[7]

The spin–spin couplings between the two strongly deshielded protons and the protons at C-1 and C-6 accord with structure **22** rather than **23.** From examination of Dreiding models, the dihedral angles between hydrogens on C-1 and C-2, and between those on C-5 and C-6, are approximately 40° in structure **22** and about 0–10° for structure **23.** The vicinal coupling constants predicted[8] for these dihedral angles would be near 5.9 c.p.s. for **22,** in good accord with the experimental values of 5.4 and 6.0 c.p.s., and 9.7–10 c.p.s. for **23.**

As trifluoroacetic acid was added to a solution of the product in deuteriochloroform, the signals at τ 4.7

(6) See references cited in P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.,* **86,** 1171 (1964).

(7) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p. 115 ff.

(8) K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.,* **83,** 4623 (1961).

and 6.0 diminished in relative intensity, additional peaks at τ −0.2, 1.0, and 4.4 developed, and the rest of the spectrum was only slightly modified. Addition of more than 1 equiv. of trifluoroacetic acid influenced the chemical shift of the proton at τ −0.2 but produced no further change in the spectrum; the signals at τ −0.2, 1.0, and 4.4 each corresponded to one proton in relative intensity. Upon addition of deuterium oxide, the peak at τ −0.2 disappeared, while those at 1.0 and 4.4 remained.

These n.m.r. results may be readily correlated with structure 24, the conjugate acid of 22.

24   25
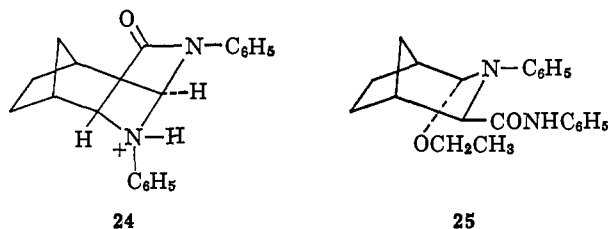
Ethanolysis of 22 gave a compound $C_{22}H_{26}N_2O_2$, assigned structure 25. That the compound is a secondary amide rather than an ester or a tertiary amide–amine is obvious[9] from its infrared bands at 3300, 3070, 1665, and 1550 cm.$^{-1}$. The n.m.r. spectrum showed doublets at τ 5.1 and 5.8, assigned to the O–CH–N and C–CH–N protons, and one proton at 0.01.

Reduction of 22 with lithium aluminum hydride gave two colorless oils. The first, $C_{20}H_{22}N_2$, showed no N–H stretching vibrations in the infrared and an n.m.r. spectrum with deshielded protons at τ 4.86 (1 H), 6.1 (1 H), and 6.8 (2 H). These analytical and spectral data are in agreement with structure 26 for the reduction product; the deshielded protons are assigned as tertiary hydrogens adjacent to two nitrogens (at 4.86) or one nitrogen (6.1), and methylene hydrogens adjacent to a nitrogen atom (at 6.8). The second product, obtained in insufficient amounts for complete characterization, showed bands in its infrared spectrum indicative[10] of a secondary aliphatic–aromatic amine (3430, 1315, and 1260 cm.$^{-1}$); structure 27 is tentatively assigned to this material.

26   27
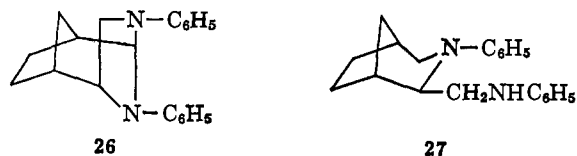
The mass spectral data for the $C_{20}H_{20}N_2O$ adduct summarized in Table I are in agreement with its formulation as 22. The interpretation of the data given in Chart I is supported in part by analogy[11] and in part by observation of the calculated metastable ion peaks as shown.

Thus, we conclude from the satisfactory agreement between the observed spectral and chemical properties of the $C_{20}H_{20}N_2O$ adduct and the properties which

(9) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, pp. 42–46.
(10) Reference 9, p. 38.
(11) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 5; A. M. Duffield, H. Budzikiewicz, D. H. Williams, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 810 (1965).

Chart I. Rationalization of Mass Spectrum of $C_{20}H_{20}N_2O$ Adduct
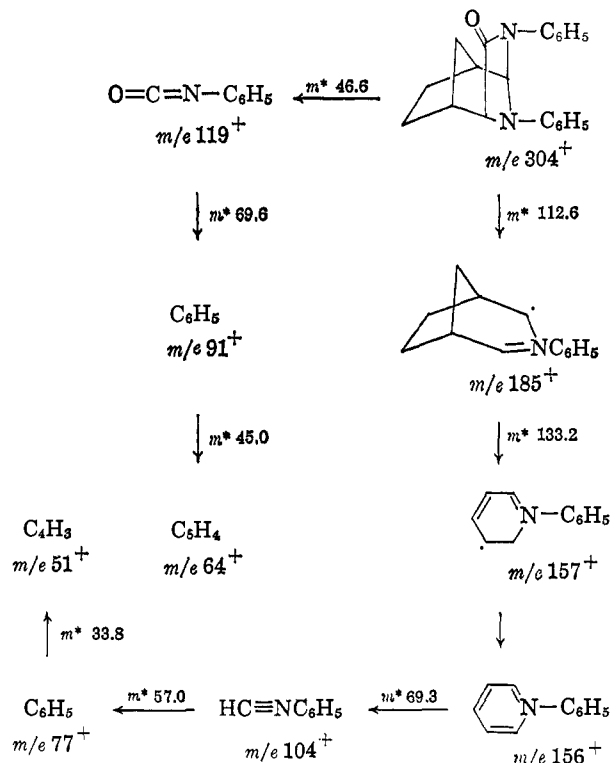
would be predicted for structure 22 that a structural assignment is warranted. The adduct of m.p. 162–163° derived from the triazoline 4 and phenyl isocyanate is the rearranged tricyclic lactam 22, a 4,10-diphenyl-4,10-diazatricyclo[4.2.1.1^{2,5}]decan-3-one.

Table I. Principal Mass Spectral Peaks of $C_{20}H_{20}N_2O$ Adduct

| Ionizing electron voltage, e.v. | Relative intensities | | | | | | | | | |
| | *m/e* | | | | | | | | | |
	304 (M)	185	157	156	119	104	91	77	64	51
15	100	32			4					
40	54	77	40	37	100					
70	11	16	19	33	30	27	20	100	27	27

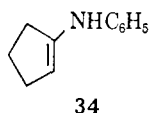## Mechanistic Postulate

Among the several mechanistic schemes that might be considered adequate to explain the formation of adducts 8 and 22, we currently favor one outlined below. It is based on the knowledge that Δ^2-1,2,3-triazolines,

31   32   33
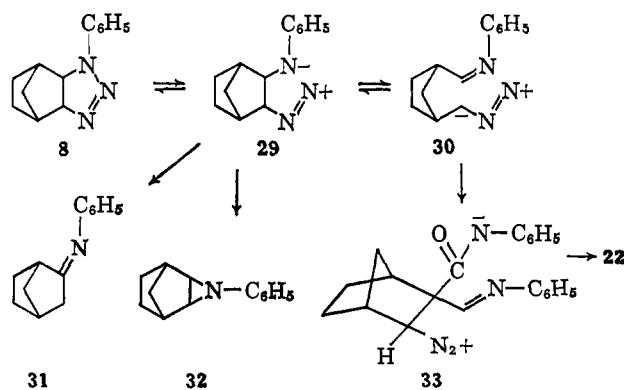
cycloaddition products from olefins with azides or from anils with diazoalkanes, decompose thermally to

give anils and diazoalkanes as cycloelimination products.[12] In this postulated mechanism, the triazoline may dissociate stepwise and reversibly through cleavage of first an N–N bond and then a C–C bond. Loss of nitrogen from one or both of these bipolar species may lead to aziridines or anils, the dominant products in the absence of phenyl isocyanate.[13] In the case of triazoline 1, a hydrogen migration with the loss of nitrogen could give the enamine 34 which in the presence of phenyl isothiocyanate would be expected[14] to give the thiocarbanilide 8. Reaction between 30 and phenyl isocyanate could proceed through an obvious pathway formally involving 33 to give the observed product. Intermediates analogous to 29 have been suggested previously[13b] for triazoline decompositions.

34

This mechanistic postulate serves to indicate at least one manner in which 8 and 22 could be formed and provides a conceptual framework to guide further research on these reactions.

Conclusions

The structural assignments for products 8 and 22 made above emphasize a need for caution in interpreting reactions according to a presumed mechanistic formula. Many two- + three → five-membered ring cycloaddition reactions may occur without the intervention of 1,3-dipolar intermediates, even though in some of these reactions 1,3-dipolar intermediates may seem plausible.[15]

Experimental[16]

4-Phenyl-2,3,4-triazabicyclo[3.3.0]oct-2-ene (1) was prepared from phenyl azide and cyclopentene; after two recrystallizations from 1:1 pentane–hexane it had m.p. 53° (lit.[17] 53°).

Reaction of 4-Phenyl-2,3,4-triazabicyclo[3.3.0]oct-2-ene (1) *with Phenyl Isothiocyanate.* In a 100-ml. three-necked flask, which was fitted with a thermometer and a reflux condenser connecting through an Ascarite trap to an inverted graduate nitrogen collector, 3.454 g. (0.0185 mole) of the triazoline 1, 14 g. (0.1 mole) of phenyl isothiocyanate, and 29 ml. of chlorobenzene were stirred magnetically and heated to 110–111°. The nitrogen evolved was collected over water; the data obtained corresponded to good first-order kinetics through three half-lives ($k_1 = 2.6 \pm 0.3 \times 10^{-4}$ sec.$^{-1}$).

(12) G. D. Buckley, *J. Chem. Soc.*, 1850 (1954).
(13) (a) P. Scheiner, *J. Org. Chem.*, 30, 7 (1965); (b) A. L. Logothetis, *J. Am. Chem. Soc.*, 87, 749 (1965).
(14) G. A. Berchtold, *J. Org. Chem.*, 26, 3034 (1961); S. Hünig, K. Hübner, and E. Benzing, *Chem. Ber.*, 95, 926 (1962); R. Fusco, G. Bianchetti, and S. Rossi, *Gazz. chim. ital.*, 91, 825 (1961).
(15) See, for instance, paper II of this series; P. Yates and T. J. Clark, *Tetrahedron Letters*, No. 13, 435 (1961); N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *J. Org. Chem.*, 29, 3383 (1964), and subsequent papers; W. Ried and R. Dietrich, *Ann.*, 666, 113 (1963); W. J. Linn, *J. Am. Chem. Soc.*, 87, 3665 (1965).
(16) Analyses are by J. Nemeth and associates, Urbana, Ill. Melting points are uncorrected. Perkin-Elmer Model 521 or 237, Varian A-60 or Varian V-4300B, equipped with a superstabilizer, Cary 14, and Atlas CH-4 spectrometers, were used for determining infrared, nuclear magnetic resonance, ultraviolet, visible, and mass spectra.
(17) K. Alder, G. Stein, and W. Friedrichsen, *Ann.*, 501, 38 (1933).

The chlorobenzene and excess phenyl isothiocyanate were removed at reduced pressure. An attempt to dissolve the residue in 40 ml. of boiling cyclohexane caused yellow crystals to separate exothermically. The crystals were collected, washed, and dried to give 4.25 g. (78%) of product, m.p. 125–130° dec. Recrystallization from cyclohexane gave material, m.p. 128.5–130.5°; $\lambda_{max}^{CHCl_3}$ 386 mμ (ϵ 24,000) and 314 mμ (ϵ9000); $\nu_{max}^{CHCl_3}$ 3390, 1612, 1595, 1580, 1500, 1390, and 1250 cm.$^{-1}$ (strong).

Anal. Calcd. for $C_{18}H_{18}N_2S$: C, 73.45; H, 6.16; N, 9.52; mol. wt., 294. Found: C, 73.36; H, 6.12; N, 9.39; mol. wt., 296 (osmometric in benzene).

The n.m.r. spectrum of this adduct had peaks at τ −3.0 (1 H), 2.0–3.4 (11 H), a multiplet centered at 7.25 (4 H), and a multiplet centered at 8.15 (2 H).

2-Oxocyclopentylthiocarbanilide (9) was prepared *via* the cyclopentanone–morpholine enamine 10[18] and 2-morpholinocyclopentenylthiocarbanilide (11), m.p. 123–125° (lit.[5] m.p. 122°), following the method of Reid and Käppeler.[5] It was recrystallized from cyclohexane and had m.p. 92.5–94° (lit.[5] m.p. 94°).

Hydrolysis of Adduct 8. A mixture of 1.04 g. of the adduct 8 in 5.9 ml. of concentrated sulfuric acid and 4.1 ml. of water was kept in an icebox overnight. In the morning it was allowed to stand at room temperature, with occasional shaking, for 90 min. The resulting homogeneous solution was poured onto chipped ice. A yellow plastic material was collected and dried; recrystallization from 27 ml. of cyclohexane gave 0.454 g. (63%) of 2-oxocyclopentylthiocarbanilide (9), m.p. 93.5–94.5° (lit.[5] m.p. 94°), identified by comparison of its infrared and n.m.r. spectra with those of an authentic sample. The mixture melting point of the authentic and derived compounds was 93–95°.

The aqueous acidic mother liquor saved when the crude 9 was collected was made basic with sodium hydroxide and treated with 0.6 g. of benzoyl chloride. The solid product obtained (0.495 g., 71% of theory) was recrystallized from ethanol and had m.p. 160.0–161.5°. Its infrared spectrum was identical with that of authentic benzanilide of m.p. 160.0–161.5°; the mixture melting point of the authentic and derived samples showed no depression.

Phenyl Azide–Norbornene Adduct (4). A solution of phenyl azide (16.0 g., 0.134 mole) and norbornene (20.0 g., 0.213 mole) was allowed to stand in the dark. The reaction was completed within a few minutes; the crystalline product was recrystallized twice from methanol to give needles of m.p. 100–101° (lit.[19] m.p. 101–102°) in 98% yield.

Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.20; H, 7.01; N, 19.63.

Adduct from Phenyl Isocyanate and Triazoline 4. Into a 100-ml. round-bottomed flask were placed 1.0 g. of triazoline 4, 16.0 g. of phenyl isocyanate, and 20.0 g. of dry *o*-dichlorobenzene. The flask contents were heated to 155–160° for 2–3 hr.

The excess phenyl isocyanate and *o*-dichlorobenzene were removed until about 2 ml. of residue remained. Addition of 2 ml. of cyclohexane and scratching with a glass rod caused rapid crystal formation. The

(18) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkoviez, and R. Terrell, *J. Am. Chem. Soc.*, 85, 207 (1963).
(19) G. Komppa and S. Beckman, *Ann.*, 512, 172 (1934).

material was recrystallized twice from cyclohexane and had m.p. 162–163° (60% yield); ν_{max}^{KBr} 1700 cm.$^{-1}$; λ_{max}^{EtOH} 245 mμ (log ϵ 4.4). Recrystallization from ethyl acetate gave a polymorph of m.p. 172–173°.

Anal. Calcd. for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.69; H, 6.62; N, 9.19.

The n.m.r. spectrum of the product in deuteriochloroform showed absorptions at τ 2.4–3.4 (10 H), 4.7 (1 H), 6.0 (1 H), 7.2–7.6 (2 H), and 8.0–8.8 (6 H).

Double resonance n.m.r. experiments run with field-sweep operation were employed to study the nature of the coupling of the protons with peaks at τ 4.7 and 6.0.

When ($\omega_1 - \omega_2$) was 150 c.p.s., the peak at τ 4.7 became a doublet with a coupling constant of 2.3 c.p.s., while the peak at 6.0 remained a quartet. When ($\omega_1 - \omega_2$) was 82 c.p.s., the peak at τ 4.7 was observed as a doublet with a coupling constant of 5.4 c.p.s. and the peak at 6.0 became a doublet with a coupling constant of 2.3 c.p.s.

The over-all result of the double resonance n.m.r. work was that the protons at τ 4.7 and 6.0 are coupled with each other ($J = 2.3$ c.p.s.) and that they are each coupled to a proton at 7.2–7.6 with $J = 5.4$ and 6.0 c.p.s.

The n.m.r. spectrum of this adduct in chloroform-trifluoroacetic acid and its mass spectrum are reported above.

Attempted catalytic hydrogenation of 0.38 g. of the $C_{20}H_{20}N_2O$ product with 34 mg. of platinum oxide in glacial acetic acid at atmospheric pressure for 4 hr. resulted in no consumption of hydrogen.

Ethanolysis of Adduct 22. Compound 22 (0.444 g.) was dissolved in 40 ml. of 10% potassium hydroxide–95% ethanol solution and refluxed for 2 hr. The cooled reaction mixture was diluted with water and extracted with ether. The ethereal extract was dried and concentrated to give a crystalline residue which was recrystallized twice from ethanol–water; the product had m.p. 150–152° (0.204 g., 40% of theory).

Anal. Calcd. for $C_{22}H_{26}N_2O_2$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.43; H, 7.48; N, 7.99.

This colorless solid had $\nu_{max}^{CHCl_3}$ 3300, 3070 (w), 2955, 1665, 1600, 1550, 1450, 1270 (m), 1250 (m), and 1055 cm.$^{-1}$.

Its n.m.r. spectrum showed absorptions at τ 0.01 (1 H), 2.3–3.4 (10 H), 5.1 (1 H), 5.8 (1 H), 6.3 (2 H), and 7.0–7.9 (11 H).

Lithium Aluminum Hydride Reduction of 22. To a magnetically stirred solution of 0.496 g. of lithium aluminum hydride in 30 ml. of dry tetrahydrofuran under an argon atmosphere was added a solution of the $C_{20}H_{20}N_2O$ adduct (22) (0.281 g.) in 20 ml. of tetrahydrofuran over a 20-min. period. The reaction mixture was refluxed for 3.5 hr., cooled, and decomposed by cautious addition of water and 15% aqueous sodium hydroxide. Filtration, ether extraction of the filtrate, and drying, filtration, and concentration of the ethereal solution gave a residue which was purified by g.l.p.c. on a 0.6-m. SE-30 silicone rubber column at 230°. The major component was collected as a colorless oil.

Anal. Calcd. for $C_{20}H_{22}N_2$: C, 82.76; H, 7.59. Found: C, 82.10; H, 7.71.

The oil had $\nu_{max}^{CHCl_3}$ 3100–2800 (m), 1600 (s), 1500 (s), 1060 (w), and 990 cm.$^{-1}$ (w); its n.m.r. spectrum showed absorptions at τ 2.8–3.65 (10 H), 4.86 (1 H), 6.1 (1 H), 6.8 (2 H), and 7.3–9.0 (8 H).

A minor product was isolated by g.l.p.c. on a 1-m. XF-1150 column at 150° as a colorless oil; ν_{max}^{neat} (selected) 3430, 3100–2800, 1610, 1510, 1470, 1445, 1420, 1315, 1260, 1145, and 1170 cm.$^{-1}$ (all s or m).

The Synthesis and the Decomposition of cis- and trans-3,5-Bis(p-anisyl)-1-pyrazolines[1]

C. G. Overberger, N. Weinshenker,[2] and J-P. Anselme

Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York. Received May 5, 1965

The isolation and the characterization of cis- and trans-3,5-bis(p-anisyl)-1-pyrazolines are reported and their n.m.r. spectra are interpreted. A mechanism for the formation of the two isomers is suggested. Their thermolysis and their photolysis have been studied, and the possible pathways of these decompositions are discussed.

Introduction

As part of our general interest in aliphatic azo compounds, the chemistry of medium-sized cyclic azo compounds has been investigated over a number of years. In the latest papers in the series,[3a–c] the synthesis and the stereospecific decomposition of trans-3,5-diaryl-1-pyrazolines (I) were described. More recently, a preliminary communication from this laboratory[4] reported the isolation and the characteriza-

(1) This is the 44th paper in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper, see C. G. Overberger and J-P. Anselme, *J. Am. Chem. Soc.*, 86, 658 (1964).

(2) This paper comprises a portion of a thesis submitted by N. Weinshenker in partial fulfillment of the requirements for the B.S. degree, 1964.

(3) (a) C. G. Overberger and J-P. Anselme, *J. Am. Chem. Soc.*, 84, 869 (1962); (b) C. G. Overberger, J-P. Anselme, and J. R. Hall, *ibid.*, 85, 2752 (1963); (c) C. G. Overberger and J-P. Anselme, *ibid.*, 86, 658 (1964).

(4) C. G. Overberger, N. Weinshenker, and J-P. Anselme, *ibid.*, 86, 5364 (1964).