

1,3-Dipolar Cycloaddition Reactions of Aziridines onto 1,2,3-Triphenylcyclopropene

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1,3-Dipolar cycloaddition reactions of 1-cyclohexyl- and 1-methyl-2-aryl-3-phenylaziridines (2)–(7) with 1,2,3-triphenylcyclopropene (1) gave 3-cyclohexyl- and 3-methyl-2-aryl-1,4,5,6-tetraphenyl-3-azabicyclo[3.1.0]hexanes (8)–(13), respectively, the configurations of which were assigned as (14) based upon comparisons of the ^1H n.m.r. spectrum of the 1 : 1 adduct (8) with that of its stereoisomer (8'). On treatment of the 3-azabicyclo[3.1.0]hexanes (8) and (13) with tetrachloro-*o*-benzoquinone, 2-benzoyl-3,4,5,6-tetraphenylpyridine (20) was obtained.

It is well documented that cycloaddition reactions with various cyclopropenes¹ and 1-azirines² are useful for the synthesis of five- or six-membered heterocycles, and that the ease of cycloaddition is strongly affected by steric factors.³ However, the reports of cyclopropene-

azomethine ylide reactions have only been for diphenylcyclopropenone (17) (DPC)⁴ and for 2-phenylazirine;⁵ no successful 1,3-dipolar cycloaddition onto 1,2,3-triphenylcyclopropene (1) (TPC) has been reported, although its Diels-Alder reactions (despite the expected large steric hindrance) have been described by several authors.^{1,6}

¹ M. L. Deem, *Synthesis*, 1972, 675.

² D. J. Anderson and A. Haddner, *Synthesis*, 1975, 483.

³ R. Huisgen, R. Grashey, and J. Sauer, in 'The Chemistry of Alkenes,' ed. S. Patai, John Wiley, New York, 1964, p. 739.

⁴ (a) J. W. Lown, T. W. Maloney, and G. Dallas, *Canad. J. Chem.*, 1970, **48**, 584. (b) For a review on cyclopropenone, see K. T. Potts and J. S. Baum, *Chem. Rev.*, 1974, **74**, 189.

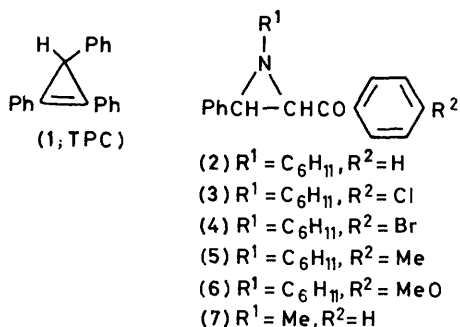
⁵ K. Matsumoto and K. Maruyama, *Chem. Letters*, 1973, 759.

⁶ (a) K. B. Wiberg, W. J. Bartley, *J. Amer. Chem. Soc.*, 1960, **82**, 6375; (b) M. A. Battiste, *Chem. Ind.*, 1961, 550; (c) M. A. Battiste, *Tetrahedron Letters*, 1964, 3795; (d) D. T. Longone and D. M. Stehoumer, *ibid.*, 1970, 1017.

This work reports that 1-cyclohexyl- and 1-methyl-2-aroil-3-phenylaziridines (2)—(7) undergo cycloaddition with TPC to give 3-cyclohexyl- and 3-methyl-2-aroil-1,4,5,6-tetraphenyl-3-azabicyclo[3.1.0]hexanes (8)—(13), respectively.

RESULTS AND DISCUSSION

A solution of the aziridine (2) and an equimolar amount of TPC were refluxed in toluene under N_2 for

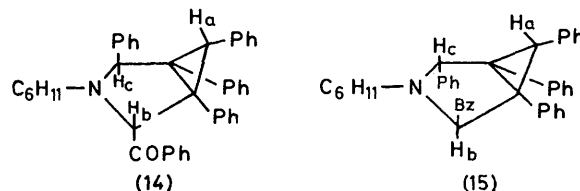


48 h, and chromatographed to give a 1 : 1 adduct (8) in 65% yield and trace amounts of its stereoisomer (8'). The i.r. spectra of (8) and (8') showed carbonyl absorptions at 1668 and 1675 cm^{-1} respectively, and their mass spectra showed the same parent peak (m/e 573). The 1H n.m.r. spectrum of (8) exhibited a singlet due to the triphenylcyclopropyl proton at δ 3.48,^{6c,7} a two-proton singlet due to the pyrrolidiny-CH at δ 5.42, and multiplets due to cyclohexyl and phenyl protons. In the ^{13}C n.m.r. spectrum of (8), the signal at δ 208.42 was assigned to the carbonyl carbon, the remaining assignments being shown in Table 2. The signal at δ 32.14 was assigned to C-6 since it was the highest field signal of the azabicyclic ring carbons. The resonances of C-2 and C-1 should appear at higher field than those of C-4 and C-5 respectively because the former are situated at positions nearer to the carbonyl than the latter,⁸ and thus the signals at δ 48.21(s), 51.13(s), 68.99(d), and 75.00(d) were assigned to C-1, C-5, C-2, and C-4, respectively. The other six

* For the stereochemistry of 1,3-dipolar cycloadditions of aziridines see ref. 9.

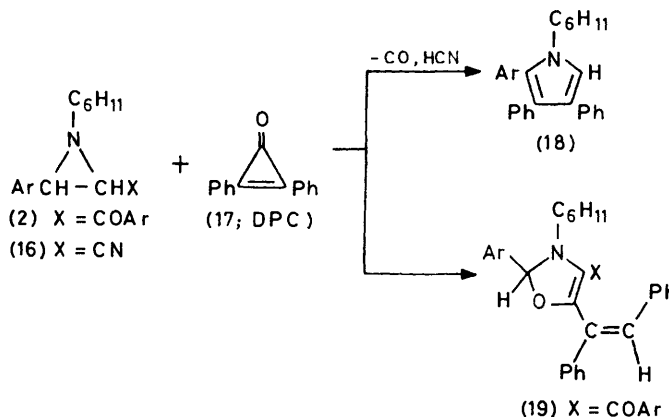
⁷ (a) C. D. DeBoer, D. H. Wadsworth, and W. C. Perkins, *J. Amer. Chem. Soc.*, 1973, **95**, 861; (b) R. Breslow and P. Dowd, *ibid.*, 1963, **85**, 2729.

non-aromatic resonances (at δ 25.73, 25.89, 26.39, 31.49, 33.44, and 56.49) are assigned to the cyclohexyl carbons, suggesting that (8) is probably a mixture of two conformational isomers in which the cyclohexyl ring is fixed either to a chair form or to a boat form on the n.m.r. time scale. The 1H n.m.r. spectrum of (8') showed three singlets at δ 4.05, 4.98, and 5.80 together with multiplets due to cyclohexyl and phenyl protons. Therefore, the configurations of (8) and (8') were tentatively assigned as (14) and (15), respectively,* by taking into consideration



that an alicyclic ring proton is shielded by *cis-vic*-phenyl or stereochemically proximate phenyl;¹⁰ the H_b resonance should appear at higher field in (8') than in (8), while the H_a and H_c resonances should appear at higher field in (8) than in (8').

Analogous reactions of *para*-substituted benzoylaziridines (3)—(6) and 2-benzoyl-1-methyl-3-phenylaziridine (7) with TPC produced the 1 : 1 adducts (9)—(13), the configurations of which [except (13)] may be regarded as the same as that of (14) because of the similar patterns to those of (8) in the i.r., 1H n.m.r., and ^{13}C n.m.r. spectra. However, no product corresponding to (15) could be isolated in any reactions, and the stereochemistry of (13) remains undetermined since its stereoisomer was not obtained. Their physical and analytical data are tabulated in Tables 1 and 2.



On the other hand, 2-cyano-1-cyclohexyl-3-arylaziridines (16) did not react with TPC in refluxing toluene or xylene. Similar reactions of (16) with DPC in refluxing xylene are reported to give 2-aryl-1-cyclohexyl-3,4-

⁸ E. Sol'aniva, S. Toma, and S. Gronowitz, *Org. Magnetic Resonance*, 1976, **8**, 439.

⁹ R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, 1967, **89**, 1753.

¹⁰ R. Sustmann, R. Huisgen, and H. Huber, *Chem. Ber.*, 1967, **100**, 1802.

diphenylpyrroles (18), hydrogen cyanide, and carbon monoxide,* or the 4-oxazoline derivative (19).^{4a,11}

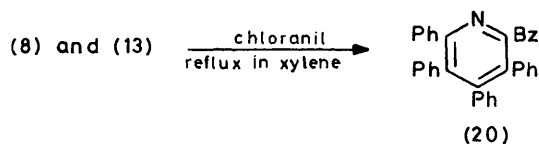
the ¹H n.m.r. spectrum, and the correct elemental analysis.

TABLE 1
Analytical and spectroscopic data of 3-azabicyclo[3.1.0]hexanes (8—13)

Compd. (formula)	Yield (%)	M.p. (°C)	Found (%) (Required, %)			M ^a	ν(CO) ^b (cm ⁻¹)	δ (CDCl ₃) ^c					
			C	H	N			cyclohexyl		ring		Aromatic	Me
								CH ₂	N-CH ^d	H _a	H _b , H _c		
(8) (C ₄₂ H ₃₉ NO)	65	179—182	88.15 (87.92)	6.95 (6.85)	2.15 (2.44)	573	1 668	0.7—2.0	2.60	3.48	5.42	6.16—7.63	
(8') (C ₄₂ H ₃₉ NO)	e	259—262				573	1 675	0.7—1.8	2.70	4.05	4.98, 5.80	6.85—7.58	
(9) (C ₄₂ H ₃₉ ClNO)	13	186—188	83.00 (82.94)	6.20 (6.30)	2.35 (2.30)	608	1 680	0.7—2.0	2.70	3.55	5.45	6.25—7.62	
(10) (C ₄₂ H ₃₉ BrNO)	23	151—155	77.05 (77.29)	5.75 (5.87)	1.90 (2.15)	652	1 664	0.6—2.0	2.71	3.58	5.46, 5.48	6.27—7.55	
(11) (C ₄₃ H ₄₁ NO)	24	203—205	87.75 (87.86)	6.90 (7.03)	2.60 (2.38)	587	1 670	0.7—2.0	2.72	3.56	5.48	6.26—7.58	2.28
(12) (C ₄₃ H ₄₁ NO ₂)	19	186—188	85.30 (85.54)	6.95 (6.84)	2.30 (2.32)	603	1 675	0.7—2.1	2.72	3.55	5.47	6.26—7.70	3.78
(13) (C ₃₇ H ₃₁ NO)	47	183—185	87.65 (87.89)	6.15 (6.18)	2.50 (2.77)	505	1 670			3.60	5.01, 5.45	6.29—7.70	2.28

^a By mass spectrometry. ^b KBr disc. ^c Integral values of each resonances were satisfactory. ^d Broad singlet. ^e Trace; elemental analysis could not be performed.

Finally, treatment of (8) and (13) with chloranil (tetrachloro-*o*-benzoquinone) in refluxing xylene produced 2-benzoyl-3,4,5,6-tetraphenylpyridine (20) with



dehydrogenation, and elimination of cyclohexane and methane, respectively. The structure of (20) was

Thus, it may be inferred that the reactivity of aroyl-aziridines is considerably higher than that of cyano-aziridines, and that TPC is a fairly effective dipolarophile. Further work is in progress on the 1,3-dipolar cycloadditions into TPC.¹²

EXPERIMENTAL

M.p.s were taken on a Yanagimoto micromelting point apparatus. I.r. spectra were obtained on a Hitachi EPI-G3 spectrometer, u.v. spectra were taken on a Hitachi 139 spectrophotometer, and ¹H n.m.r. spectra on a JEOL 4H-100 instrument (reported in p.p.m. downfield from internal

TABLE 2
¹³C N.m.r. data of 3-azabicyclo[3.1.0]hexanes (8—13) *

Compd.	C-6 (d)	C-1 (s)	C-5 (s)	C-2 (d)	C-4 (d)	C-7 (s)	CH ₃ (q)	C-9 (t)	C-10		C-8		C-7 (d)
									(t)	(t)	(t)	(t)	
(8)	32.14	48.21	51.13	68.99	75.00	208.42		25.73	25.89	26.39	31.49	33.44	56.49
(9)	32.14	48.21	51.13	68.91	74.91	207.37		25.73	25.97	26.38	31.57	33.52	56.33
(10)	32.14	48.24	51.10	68.89	74.93	207.52		25.71	25.97	26.36	31.56	33.44	56.36
(11)	32.06	48.21	51.13	68.66	74.91	207.86	21.59	25.73	25.97	26.46	31.41	33.36	56.33
(12)	31.98	48.21	51.13	68.42	74.91	206.32	55.27	25.73	25.97	26.46	31.33	33.36	56.33
(13)	32.06	47.79	51.04	73.50	78.24	204.33	34.48						

* In p.p.m. from internal SiMe₄ in CDCl₃, multiplicity in parentheses.

assigned on the basis of a peak at 1 680 cm⁻¹ in the i.r. spectrum, a parent peak at *m/e* 537 in the mass spectrum, the resonances of only aromatic protons (δ 6.73—7.98) in

* DPC reacted with 2-aryl (*o*-chloro, *p*-chloro, *p*-methyl, and *p*-methoxy-phenyl)-3-cyano-1-cyclohexylaziridines (16) in refluxing xylene for 20—24 h to give 2-aryl-1-cyclohexyl-3,4-diphenylpyrroles (18) (*o*-chloro, m.p. 72—73 °C, yield 37%; *p*-chloro, m.p. 225.5 °C, yield 68%; *p*-methyl, m.p. 198—199 °C, yield 52%; *p*-methoxy, m.p. 171.5—174.5 °C, yield 44%). The correct mass spectra and elemental analyses were obtained for these pyrroles. A similar reaction has been described by Lown *et al.*^{4a}

SiMe₄). ¹³C n.m.r. spectra were recorded on a JEOL FX-60 pulsed Fourier-transform spectrometer operating at 15.040 MHz, using 10-mm o.d. tubes, 0.1—0.2M solutions in CDCl₃, at 30 °C; chemical shifts are in p.p.m. downfield from internal SiMe₄. Partial proton decoupling was used to

¹¹ (a) J. W. Lown, R. K. Smalley, G. Dallas, and T. W. Maloney, *Canad. J. Chem.*, 1970, **48**, 89; (b) J. W. Lown and K. Matsumoto, *ibid.*, p. 3399; (c) For a review on reactions of DPC, see K. Matsumoto, *J. Synthetic Org. Chem., Japan*, 1972, **30**, 1035.

¹² K. Matsumoto and T. Uchida, *Synthesis*, 1978, 207.

distinguish between individual carbon atoms. Mass spectra were obtained on a JEOL 01SG-2 mass spectrometer.

General Procedure for 2-Aroyl-3-cyclohexyl-1,4,5,6-tetra-phenyl-3-azabicyclo[3.1.0]hexanes (8)–(12).—A solution of 2-aryol-1-cyclohexyl-3-phenylaziridine (2)–(6)¹³ (3.8 mmol) and TPC^{7b} (3.8 mmol) was refluxed in dry toluene (40 ml) under nitrogen atmosphere for 48 h. After evaporation of the solvent *in vacuo*, the product was isolated by chromatography on silica gel with n-hexane–benzene as eluant, and was recrystallized from moist ethanol.

2-Benzoyl-3-methyl-1,4,5,6-tetraphenyl-3-azabicyclo-[3.1.0]hexane (13).—2-Benzoyl-1-methyl-3-phenylaziridine (7)¹⁴ (1 g, 4.2 mmol) and TPC (1 g, 3.8 mmol) were heated under reflux in dry toluene (40 ml) for 48 h. Evaporation of the solvent *in vacuo* gave a syrup, from which the product was isolated by chromatography on silica gel with n-hexane–benzene (1:1) as eluant, and was recrystallized from light petroleum as pale yellow crystals (0.68 g, 47%).

Reaction of Cyanoaziridines (16; Ar = Ph or p-Me-C₆H₄) with TPC.—A mixture of aziridine (16) (2.2 mmol) and TPC (2.2 mmol) in dry xylene (16 ml) was refluxed for

30 h. After the usual work-up, the isolated product (m.p. 181–184 °C) was shown to be a dimer of TPC.^{7b}

2-Benzoyl-3,4,5,6-tetraphenylpyridine (20).—(i) A stirred solution of the adduct (8) and chloranil (0.5 g) in dry xylene (20 ml) was refluxed under nitrogen for 28 h. The mixture was diluted with ether, and washed with aqueous NaOH (5%), aqueous Na₂SO₃ (5%), and water. The dried (Mg-SO₄) extract was evaporated to dryness and the residue chromatographed (alumina, benzene eluant) to give a product which was recrystallized from ethanol–benzene (1:1) as white crystals (70 mg, 17%), m.p. 244.5–246 °C (Found: C, 88.6; H, 5.15; N, 3.1%; M⁺, 487. C₃₆H₂₅NO requires C, 88.68; H, 5.17; N, 2.89%; M 487); ν_{max} (KBr) 1680 cm⁻¹ (C=O), λ_{max} (CHCl₃) 253.5 nm (log ε 4.65); δ(CDCl₃) 6.73–7.98(m). (ii) Reaction of the adduct (13) (0.15 g) with chloranil (0.2 g) in dry xylene (20 ml) was worked-up as described above to afford (20) (40 mg, 28%), m.p. 244–246 °C.

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¹³ (a) N. H. Cromwell, R. D. Babson, and C. E. Harris, *J. Amer. Chem. Soc.*, 1943, **65**, 312; (b) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. J. Vanderhorst, F. W. Olson, and J. H. Anglin, jun., *ibid.*, 1951, **73**, 1044; (c) J. W. Lown, G. Dallas, and T. W. Maloney, *Canad. J. Chem.*, 1969, **47**, 3557.

¹⁴ N. H. Cromwell and J. A. Caughlan, *J. Amer. Chem. Soc.*, 1945, **67**, 2235.