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1,3-DIPOLAR CYCLOADDITIONS OF ANHYDRO 1-PHENYLIMINO-2,4,5-TRIPHENYL-1,2,3-TRIAZOLIUM HYDROXIDE

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Abstract— Anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide (**3**), the oxidation product of benzil bisphenylhydrazone (**1**) gave 1:1-cycloadducts with a wide variety of acetylenic and olefinic dipolarophiles, yielding pyrazolino[2,3-c] and dihydropyrazolino[2,3-c] [1,2,3]-triazoles. With phenyl isocyanate and phenyl isothiocyanate **3** gave 1,3,3a,4,6-pentaphenyl-1,2,4-triazolidono[1,5-c] [1,2,3] triazol-5-one and the corresponding thione, respectively. The initially formed cycloadduct in the case of carbon disulphide fragmented to give 2,4,5-triphenyl-1,2,3-triazole. The same triazole was obtained in the thermal decomposition of the cycloadducts obtained from the reaction of **3** with dimethyl maleate and dimethyl fumarate. Kinetic studies indicate that these addition reactions are examples of concerted 1,3-dipolar cycloadditions.

CONSIDERABLE controversy exists in the literature concerning the structure of the oxidation products of bisphenyl and bisbenzoylhydrazones of 1,2-diketones.[1] Pechmann[2] had reported that the oxidation of bisphenylhydrazones of 1,2-diketones gives intensely coloured substances, which were designated as 2,3-dihydro-1,2,3,4-tetrazines. The oxidation of bisbenzoylhydrazones of 1,2-diketones, on the other hand, gave colourless products which were also assumed to be dihydrotetrazine derivatives. Subsequent studies[3-5] have shown that the products of oxidation of bisphenylhydrazones derived from 1,2-diketones are in fact bisphenylazoolefins and not dihydrotetrazines. Curtin *et al.*[6, 7] have reported that the corresponding products of oxidation of bisbenzoylhydrazones of 1,2-diketones are correctly represented as enol benzoates. These enol benzoates undergo ready rearrangement to dibenzoyl derivatives of N-aminotriazoles, presumably through a 4-membered, cyclic transition state.[8] Quite recently, Petersen and Heitzer[9] have, on the basis of high resolution NMR studies, shown that the product obtained from the oxidation of 2,3-butanedione bisbenzoylhydrazone with potassium ferricyanide exists as the mesoionic anhydro/1-benzoylimino-2-benzoyl-4,5-dimethyl-1,2,3-triazolium/hydroxide, Katritzky *et al.*[10] have questioned the assignment of such mesoionic structures for the oxidation products of bisbenzoylhydrazones. These workers, however, concede that such mesoionic structures may be probable in the case of ortho-bisazo compounds, in which one of the azo groups is electrophilically substituted.[11] They have also shown that the structure of the oxidation products of sulfonylhydrazones correspond to bisazoolefines and not either the enol benzoate or the mesoionic iminotriazole analogues.

The object of the present investigation was to examine some of the reactions of the oxidation product of benzil bisphenylhydrazone (**1**), with a view to elucidating its

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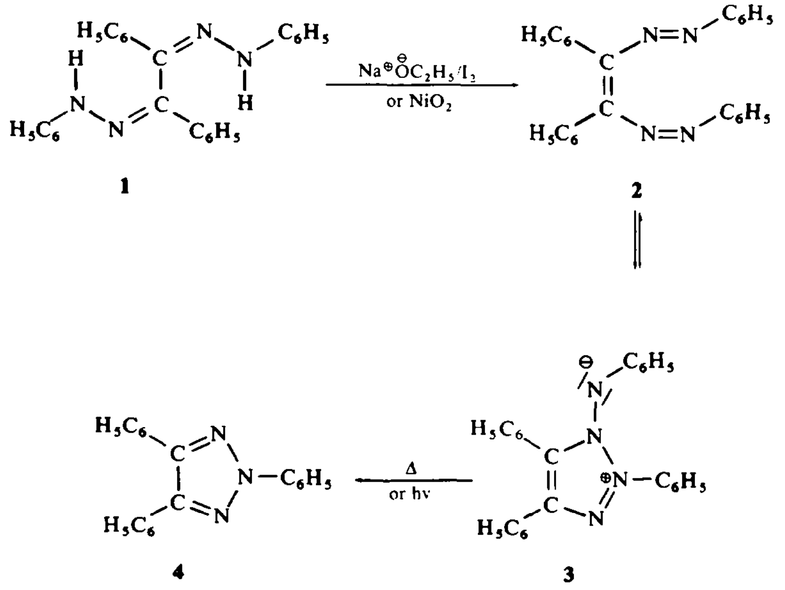
structure. Bisphenylazostilbene (**2**) has been reported as one of the products of oxidation of benzil bisphenylhydrazone, when a mixture of sodium ethoxide and iodine[12] or nickel peroxide[13] was used as the oxidizing agent. On the other hand, when manganese dioxide[14] was employed, the major product of oxidation was 2,4,5-triphenyl-1,2,3-triazole (**4**). The same triazole was formed both in the thermal and photochemical fragmentation[15, 16] of the oxidation product of benzil bisphenylhydrazone. The formation of the triazole in these reactions would indicate that the oxidation product of benzil bisphenylhydrazone may be represented as the mesoionic anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide (**3**). Katritzky *et al.*[11] have pointed out that compounds analogous to the anhydro iminotriazolium hydroxides should not have intense colours as against the fully conjugated bisazoolefines. It is therefore possible that the oxidation product of benzil bisphenylhydrazone exists in thermal equilibrium between the bisphenylazostilbene form (**2**) and the mesoionic anhydro 1-phenylimino-2,4,5-triphenyl-1,2,3-triazolium hydroxide form (**3**) as shown in Scheme 1.

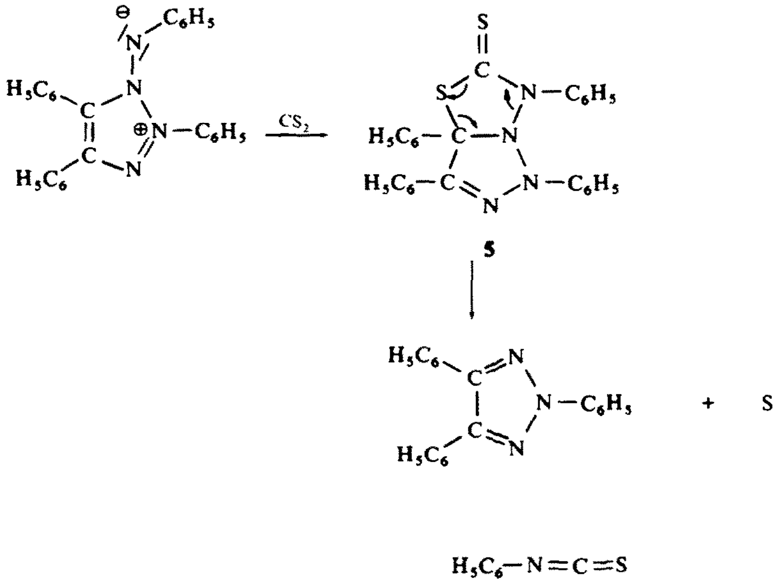
SCHEME 1



The mesoionic structure **3** represents an azomethineimine system and as such it should be capable of undergoing 1,3-dipolar cycloaddition reactions. In a preliminary communication, we have reported some of the cycloaddition reactions of **3** with different dipolarophiles.[17] During the course of the present studies we have examined in detail several of these addition reactions with a view to understanding some of the structural features of these adducts and the mechanism of these additions.

Treatment of **3** with carbon disulphide at room temperature gave a 93% yield of 2,4,5-triphenyl-1,2,3-triazole (**4**). In addition, a 83% yield of elemental sulphur and 66% yield of phenyl isothiocyanate were also isolated from this reaction. The formation of these products can be rationalized in terms of the fragmentation of an initially formed cycloadduct **5** (Scheme 2). It is interesting to note that similar loss of elemental sulphur from other sulphur containing heterocyclics has also been reported.[18]

SCHEME 2



The reaction of **3** with dimethyl acetylenedicarboxylate in refluxing acetone gave a 83% yield of a 1:1 adduct, m.p. 184° and identified as 1,3,3a,6-tetraphenyl-4,5-dicarbomethoxypyrazolino[2,3-c] [1,2,3]triazole (**7a**). The NMR spectrum of **7a** showed two sharp singlets at 3·46 ppm (3H) and 3·66 ppm (3H), respectively due to the two ester methyl protons. The phenyl protons appeared as three distinct groups of multiplets centred around 6·74 ppm (14H), 6·96 ppm (4H) and 7·29 ppm (2H), respectively.

Similarly, the reaction of **3** with methyl propiolate gave a 78% yield of a single product, m.p. 196° and identified as 1,3,3a,6-tetraphenyl-4-carbomethoxypyrazolino-[2,3-c] [1,2,3]triazole (**7b**).*[19] In the reaction of **3** with dibenzoylacetylene, however, a 64% yield of the 1:1-adduct, namely, 1,3,3a,6-tetraphenyl-4,5-dibenzoylpyrazolino-[2,3-c] [1,2,3]triazole (**7c**) was obtained (Scheme 3).

In continuation of our studies, we have examined the reactions of **3** with several olefinic substrates, with a view to understanding the stereochemical outcome of these reactions. Treatment of **3** with dimethyl maleate in acetone medium gave a 79%

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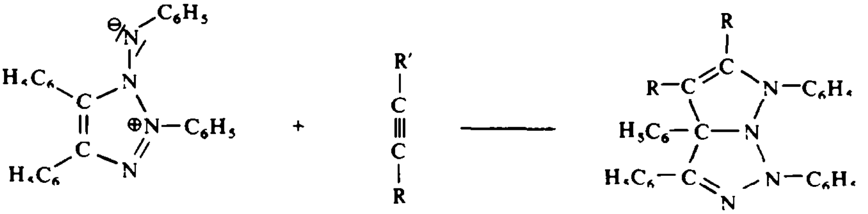
* The structure of this adduct is assumed to be **7b**, on the basis of analogy to the adduct obtained from the reaction of N,C-diphenylnitrileimine with methyl propiolate.

yield of a single isomer of the 1:1-adduct and identified as *cis*-4,5-dicarbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c] [1,2,3]triazole. The structure of this adduct was derived from analytical results and spectral data. The NMR spectrum shows two sharp singlets at 3·69 ppm and 3·07 ppm due to the ester methyl protons. The two tertiary protons appear as two sets of doublets, at 3·88 ppm and 4·41 ppm ($J = 9{\cdot}7$ Hz). The dihedral angle calculated from the observed coupling constant turns out to be around 22°, indicating thereby that the two tertiary protons are *cis* with respect to each other as would be expected in a stereospecific addition. The phenyl protons appear as three sets of multiplets at 6·67 ppm (14H), 7·17 ppm (4H) and 8 ppm (2H) ax in the case of **7a**.

SCHEME 3



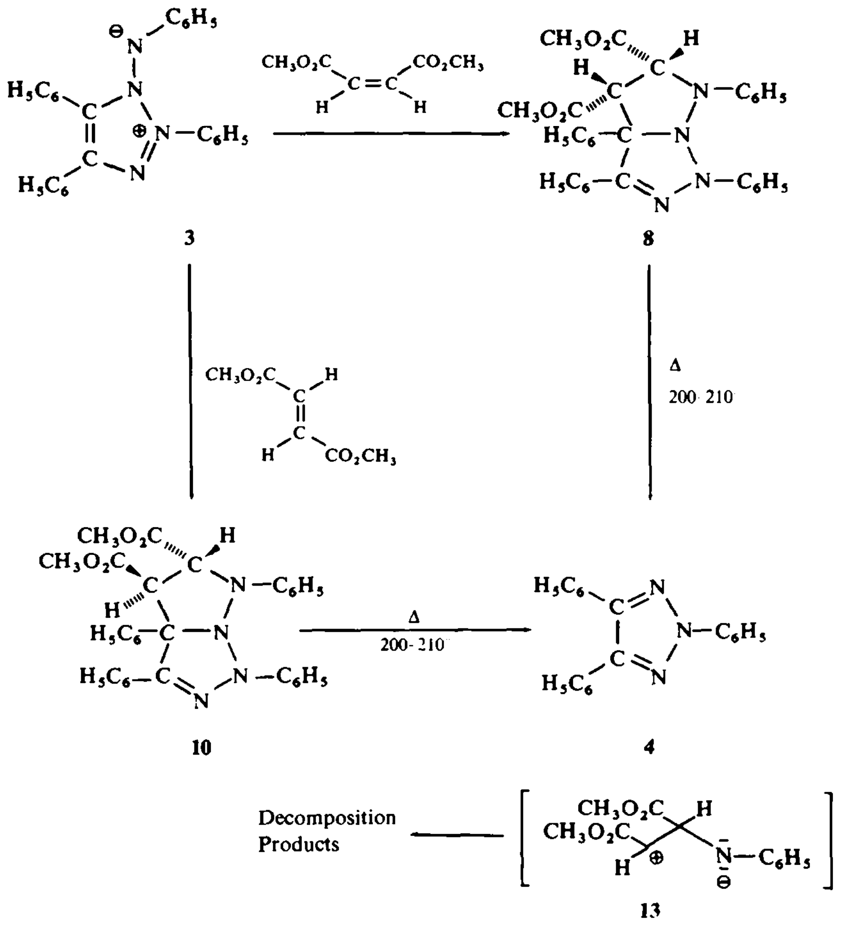
6a: $R = R' = CO_2CH_3$
b: $R = H, R' = CO_2CH_3$
c: $R = R' = COC_6H_5$

7a: $R = R' = CO_2CH_3$
b: $R = H, R' = CO_2CH_3$
c: $R = R' = COC_6H_5$

In the reaction of **3** with maleic anhydride, a 72% yield of the 1:1-adduct, 1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c] [1,2,3]triazole-4,5-dicarboxylic anhydride (**9**) was obtained. On the other hand, treatment of **3** with dimethyl fumarate gave the stereospecific *trans*-addition product, namely, *trans*-4,5-dicarbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c] [1,2,3]triazole (**10**). Similarly, the reaction of **3** with methyl crotonate and *trans*-dibenzoylethylene gave the corresponding cycloadducts **11** and **12**, respectively. The coupling constants between the two tertiary protons at 4- and 5-positions in the adducts **10**, **11** and **12** range between 5·0 and 6·5 Hz and the calculated values for the dihedral angles lie between 95 and 105°, as would be expected for these adducts with *trans* geometry.

We have also examined briefly the thermal decompositions of both **8** and **10**, the adducts obtained in the reaction of **3** with dimethyl maleate and dimethyl fumarate, respectively with the hope of obtaining some information regarding the structural details of these adducts. Heating **8** to about 200° for 15 min resulted in the formation of a 83% yield of 2,4,5-triphenyl-1,2,3-triazole (**4**). Similarly, **10** on thermolysis gave a 65% yield of **4**. A probable route to the formation of **4** from these adducts is shown in Scheme 4. Under pyrolytic conditions these adducts may be undergoing a cycloreversion reaction, giving rise to the triazole **4** and the dipolar intermediate **13**. Our attempts to trap the intermediate **13**, however, have been unsuccessful. It is probable that under the conditions of thermolysis, **13** may be undergoing further decomposition to intractable products.

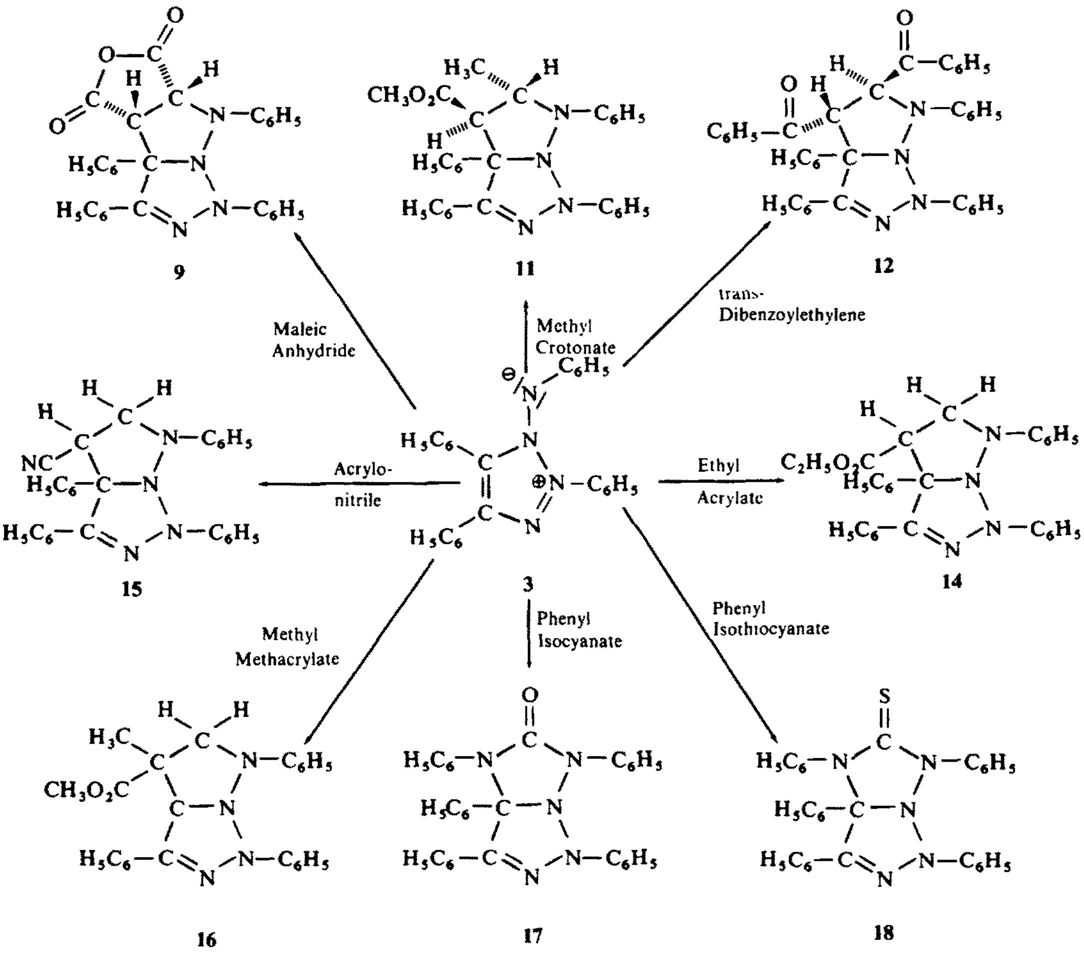
SCHEME 4



In order to find out whether there is any preferred orientation in these cycloadditions we have examined the reaction of **3** with ethyl acrylate and acrylonitrile. Treatment of **3** with ethyl acrylate and acrylonitrile gave the corresponding cycloadducts **14** and **15**, in 76% and 82%, respectively. The NMR spectrum of **14** showed a triplet at 0·7 ppm (3H) due to the Me protons of the ester ethoxyl group and a complex pattern of multiplets (5H) in the range of 3·7–6·5 ppm. The NMR spectrum of **15**, on the other hand, showed three quartets at 4·1 ppm (1H), 4·7 ppm (1H) and 5·5 ppm (1H), respectively. The signals at 4·1 ppm and 4·7 ppm were assigned to the geminal protons at C_5 and the signal at 5·5 ppm, to the tertiary proton at C_4.

Similarly, the reaction of **3** with methyl methacrylate gave 4-methyl-4-carbomethoxy-1,3,3a,6-tetraphenyl-4,5-dihydropyrazolino[2,3-c] [1,2,3]triazole (**16**). The NMR spectrum of **16** showed two singlets at 1·54 ppm (3H) and 3·08 ppm (3H) due to the Me group and the carbomethoxyl group respectively at C_4. The geminaly coupled protons at C_5 appeared as two separate doublets at 3·53 ppm and 4·59 ppm

SCHEME 5



(J = 11·48 Hz), respectively. The NMR spectrum of **16** is in full agreement with the assigned structure. It is therefore to be concluded that the nitrogen end of the azomethineimine dipole (**3**) gets itself attached to the β-carbon of the dipolarophiles such as ethyl acrylate, acrylonitrile and methyl methacrylate, giving rise to the adducts **14**, **15** and **16**, respectively (Scheme 5). The preferred orientation in the addition of **3** with different dipolarophiles is in tune with the earlier observations of Huisgen and coworkers[19, 20] concerning the orientations in the cycloadditions of related systems.

In continuation of our studies, we have examined the reactions of **3** with phenyl isocyanate and phenyl isothiocyanate. Treatment of **3** with phenyl isocyanate gave a 50% yield of 1,3,3a,4,6-pentaphenyl-1,2,4-triazolidino[1,5-c] [1,2,3]triazol-5-one (**17**), m.p. 238°. Under similar conditions, the reaction of **3** with phenyl isothiocyanate gave a 60% yield of the corresponding thione derivative **18**. The IR spectrum of **17** showed absorption bands at 1710 and 1590 cm^{-1}, characteristic of a 5-membered cyclic ureide, whereas the spectrum of **18** showed bands at 1574 and 1475 cm^{-1}, respectively, characteristic of 5-membered cyclic thioureides.[21]

The IR spectra of pyrazolino-[2,3-c] [1,2,3]triazoles (**7a–c**) and 4,5-dihydropyrazolino-[2,3-c] [1,2,3]triazoles (**8–12** and **14–16**) are similar in many respects. Table 1 summarizes the prominent absorption peaks in these adducts and their assignment to various modes of vibrations. These absorption bands are in conformity with the characteristic vibrational bands reported for fused 5-membered heterocyclic rings.[22–28]

TABLE 1. IR SPECTRAL CHARACTERISTICS OF PYRAZOLINO-[2,3-c] [1,2,3]TRIAZOLES AND 4,5-DIHYDROPYRAZOLINO-[2,3-c] [1,2,3]TRIAZOLES OBTAINED IN THE CYCLOADDITION OF ANHYDRO 1-PHENYLIMINO-2,4,5-TRIPHENYL-1,2,3-TRIAZOLIUM HYDROXIDE TO VARIOUS DIPOLAROPHILES

	IR spectral bands (KBr) cm^{-1}										
Compound	C—H Stretching	Ester C=O	C—H Bending and/or C=N stretching	Ring bending vibrations			In-plane C H deformation and ring breathing modes			Out-of-plane C—H deformations	
7a		1725	1675	1570	1480	1450	1245			775	760
7b		1730	1670	1575	1480	1480	1240			775	755
7c		1675[a]	1575	1490	1420	1310	1160	1010	950	770	730
9	2950	1730	1590	1490	1455	1320	1200	1155	975	770	750
9		1850*b* 1790*b*	1585	1490	1450	1325	1190	1150	975	770	755
10	2990, 2890	1730	1590	1475	1450		1100	1030		775, 760	750
11		1720	1570	1475	1440	1360	1205	1025			730
12		1690		1500	1400			990		785, 765	
14	2990, 2880	1720	1600, 1500	1490	1460		1110	950		770	750
15	2950, 2850	2210[c]	1535	1475	1450, 1430			1045	975	770	
16		1725	1610								

[a] This band is assigned to the C=O group of the benzoyl group.

[b] Bands due to the C=O groups of five-membered, dicarboxylic anhydrides.

[c] Band due to C≡N stretching vibration.

In order to study the mechanistic details concerning the addition reactions of **3** with different dipolarophiles, we have examined the kinetics of some of these additions. The anhydro iminotriazolium hydroxide (**3**), probably in equilibrium with the bisphenylazostilbene, shows an absorption maximum at 404 nm (ε, ~ 10^4) whereas the dipolarophiles or the adducts do not show any absorption in this region. Hence we could conveniently follow the progress of the addition reaction spectrophotometrically, by measuring the rate of decrease in intensity of this absorption maximum. In each case, a known excess (800–1000 times) of the dipolarophile was taken. Plots of the logarithm of optical density against time gave very good straight lines.* The pseudo-first order rate constants were determined from the slopes of these lines and the second order rate constants were computed from these results. The values of enthalpy and entropy of activation were determined in the usual way. The kinetic data of some of these additions are summarized in Table 2.

TABLE 2. KINETIC DATA FOR THE REACTION OF ANHYDRO 1-PHENYLIMINO-2,4,5-TRIPHENYL-1,2,3-TRIAZOLIUM HYDROXIDE WITH DIFFERENT DIPOLAROPHILES

Dipolarophile	Rate constant at 30° (litre $mol^{-1}sec^{-1}$)	$\Delta H^{\ddagger} \pm 1$ Kcal mol^{-1}	$\Delta S^{\ddagger} \pm 1$ (e.u.)
(1) Dimethylacetylene-dicarboxylate	$2{\cdot}16 \times 10^{-1}$	9·0	−34
(2) Methyl propiolate	$2{\cdot}692 \times 10^{-2}$	5·6	−49
(3) Dimethyl maleate	$1{\cdot}485 \times 10^{-3}$	9·5	−36
(4) Dimethyl fumarate	$2{\cdot}59 \times 10^{-5}$	8·0	−38
(5) Ethyl acrylate	$1{\cdot}521 \times 10^{-4}$	13·5	−34
(6) Methyl methacrylate	$3{\cdot}72 \times 10^{-5}$	11·0	−37
(7) Methyl crotonate	$7{\cdot}25 \times 10^{-6}$	10·3	−34
(8) Acrylonitrile	$6{\cdot}026 \times 10^{-4}$	10·0	−42
(9) Phenyl isocyanate	$4{\cdot}21 \times 10^{-4}$	14·5	−33
(10) Phenyl isothiocyanate	$8{\cdot}913 \times 10^{-4}$	13·4	−26

As is evident from Table 2, these reactions proceed with relatively low activation energies. The rather large, negative values for the entropies of activation would suggest an ordered transition state, characteristic of concerted cycloadditions, in general. The relative rates of addition of different dipolarophiles to **3** by and large, showed similar trends as was observed in analogous dipolar species.[27] Olefinic dipolarophiles with a *trans* geometry have been reported[27a] to react faster than their *cis* isomers in 1,3-dipolar cycloaddition reactions. However, in the case of **3** we find that it is the *cis* form of the dipolarophile which is more reactive. This may be attributed to the greater steric requirements of **3**, as compared to other dipolar species. Molecular models show that the transition state leading to the formation of the *trans*-adduct is more crowded than that for the *cis*-adduct, and hence the observed slowness of the reaction with the *trans*-dipolarophile.

EXPERIMENTAL

All m.ps are uncorrected. The IR spectra were recorded on a Perkin–Elmer, Infracord, Model-137 spectrometer and electronic spectra, on a Beckmann DB-spectrophotometer. NMR traces were recorded on a Varian, HR-100 spectrometer, using TMS as internal standard.

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* For the same dipolarophile, measurements at different temperatures were made starting with the same initial concentrations so that the log of the optical density versus time gave linear plots, intersecting at zero time. This was used as a check for the accuracy of our measurements.

TABLE 3. CYCLOADDITIONS OF ANHYDRO 1-PHENYLIMINO-2,4,5-TRIPHENYL-1,2,3-TRIAZOLIUM HYDROXIDE TO ACETYLINIC AND OLEFINIC DIPOLAROPHILES

Dipolarophile	Cycloadduct	Yield %	M.p. °C	Calcd %			Found %			Uv λ_{max}, nm (ε)
				C	H	N	C	H	N	
Dimethyl acetylenedicarboxylate	**7a**	83	184	72·66	4·88	10·35	72·45	4·99	10·02	252 (49,000), 304 (48,500), 368 (6500)
Methyl propiolate	**7b**	78	196	76·28	5·08	11·87	76·32	5·10	11·79	250 (52,000), 306 (43,500), 372 (7500)
Dibenzoylacetylene	**7c**	64	193	81·02	4·82	9·00	81·14	4·81	9·10	254 (51,000), 305 (47,500), 370 (6600)
Dimethyl maleate	**8**	79	200	72·15	5·26	10·53	72·13	5·00	10·02	246 (58,000), 288 (14,000), 332 (5600)
Maleic anhydride	**9**	71	228	74·08	4·53	11·53	74·12	4·62	11·35	246 (62,000), 290 (12,000), 330 (5400)
Dimethyl fumarate	**10**	74	205	72·15	5·26	10·53	71·91	5·33	10·61	246 (73,000), 290 (13,600), 332 (1800)
Methyl crotonate	**11**	45	203	77·32	5·52	10·05	77·54	5·54	9·99	260 (44,000), 298 (12,000), 334 (5600)
trans-Dibenzoylethylene	**12**	31	190	80·99	4·83	8·99	81·01	4·79	8·87	244 (66,000), 291 (14,000), 330 (2100)
Ethyl acrylate	**14**	79	216	76·23	5·73	11·47	76·47	5·49	11·76	256 (40,000), 298 (10,300), 324 (4500)
Acrylonitrile	**15**	82	249	78·91	5·21	15·80	78·91	5·30	15·63	250 (28,200), 288 (6700), 328 (4000)
Methyl methacrylate	**16**	54	249	77·32	5·52	10·05	77·42	5·51	10·10	258 (45,000), 296 (11,000), 328 (4500)

Starting materials. Compound 3 (73%, m.p. 179°), was prepared by the oxidation of benzil bisphenylhydrazone, as per a reported procedure.[12] Dimethyl acetylenedicarboxylate, b.p. 100° (5 mm), methyl propiolate, b.p. 80° (5 mm), dibenzoylacetylene, m.p. 110°, dimethyl fumarate, m.p. 104°, dimethyl maleate, b.p. 196°, methyl crotonate, b.p. 126°, phenyl isocyanate, b.p. 159° and phenyl isothiocyanate, b.p. 99° (15 mm) were prepared by reported procedures. Commerically available samples of maleic anhydride, *trans*-dibenzoylethylene, acrylonitrile, ethyl acrylate, methyl methacrylate and carbon disulphide were purified, either by distillation or fractional crystallization before use.

Reaction of anhydro 1-*phenylimino*-2,4,5-*triphenyl*-1,2,3-*triazolium hydroxide* (3) *with carbon disulphide*

A mixture of 3 (0·58 g, 0·0015 mol) and CS_2 (2 ml) was kept at room temp for 20 min. The unchanged CS_2 was removed under reduced pressure to give a solid, which was treated with a mixture (1 : 1) of light petroleum (b.p. 60–80°) and benzene. The insoluble residue amounted to 40 mg (83%) of elemental S, identified through its characteristic tests.

Removal of the solvent from the benzene-light petroleum soluble portion and recrystallization of the residue from light petroleum gave 0·42 g (93%) of 4, m.p. 124°. There was no depression in its m.p when mixed with an authentic sample of 4.[14]

The mother liquor after removal of the solvent was distilled under vacuum to give 100 mg (66%) of phenyl isothiocyanate which was characterized by comparison of its IR spectrum with that of an authentic sample.

Reaction of 3 *with acetylenic dipolarophiles* (**6a–c**)

In a representative run, a mixture of 0·001 mol of 3 and 0·001 mol of the dipolarophile in 2 ml acetone was refluxed for 30 min. The solid product that separated out on cooling the mixture was recrystallized from a mixture (1 : 1) of light petroleum and benzene to give the corresponding pyrazolino-[2,3-c] [1,2,3]-triazoles. Table 3 summarizes the percentage yields and the physical data of the different pyrazolino-[2,3-c] [1,2,3]triazoles (**7a–c**). NMR spectral data of these adducts are shown in Table 4.

TABLE 4. NMR SPECTRAL CHARACTERISTICS OF PYRAZOLINO AND 4,5-DIHYDROPYRAZOLINO-[2.3-c] [1.2.3]-TRIAZOLES

Cycloadduct	Aromatic* protons (20H)	$-\overset{\overset{O}{\|}}{C}-O-CH_3$ (ppm)		CH_3 (ppm)	Protons at positions C_4	C_5 (ppm)	
7a	6·96	3·66 (3H,s)	3·46 (3H,s)				
8	7·17	3·69 (3H,s)	3·07 (3H,s)		3·88 (1H,d)	4·41 (1H,d)	
10	7·16	4·43 (6H,s)			4·21 (1H,d)	5·59 (1H,d)	
11	6·88	3·23 (3H,s)		1·36(C_5) (3H,d)	3·36 (1H,d)	5·00 (1H,m)	
14	6·46	0·70[a] (3H,t)			3·12–3·79[b] (5H,m)		
15	7·00				5·50 (1H,q)	4·10 (1H,q)	4·70 (1H,q)
16	6·86	3·08 (3H,s)		1·54(C_4) (3H,s)	3·63 (1H,d)	4·59 (1H,d)	

* The aromatic protons appear as three sets of multiplets in the range of ±0·80 ppm about the ppm value indicated here.

[a] Signal due to the CH_3 of carboethoxyl group.

[b] Signal due to protons at C_4 and C_5 and methylene of carboethoxyl group. s—singlet: d—doublet, t—triplet: q—quartet: m—multiplet.

Reaction of **3** *with olefinic dipolarophiles*

In a representative run, a mixture of 0·001 mol of **3** and 0·001 mol of the dipolarophile in 2 ml acetone was refluxed for 20–30 min. Subsequent removal of acetone by distillation and recrystallization of the residue from a mixture (1 : 1) of light petroleum (60–80°) and benzene gave the corresponding 4,5-dihydropyrazolino[2,3-c] [1,2,3]triazoles. Table 3 summarizes the percentage yields and different physical data of these adducts.

Reaction of **3** *with phenyl isocyanate*

A mixture of the **3** (0·39 g, 0·001 mol) and phenyl isocyanate (0·12 g, 0·001 mol) in EtOAc (2 ml) was refluxed for 15 min. A solid residue separated out on cooling the mixture, which was recrystallized from EtOAc to give 0·25 g (48%) of **17**, m.p. 238°, as colourless crystals. (Found: C, 78·22; H, 5·00; N, 13·6. Calcd for $C_{33}H_{25}N_5O$: C, 78·11; H, 4·93; N, 13·8%). The IR spectrum of **17** showed an absorption band at 1720 cm^{-1}, characteristic of a 5-membered ureide.[21]

Reaction of **3** *with phenyl isothiocyanate*

A mixture of **3** (0·39 g, 0·001 mol) and phenyl isothiocyanate (0·14 g, 0·001 mol) was refluxed in EtOAc (2 ml) for 15 min. Work-up of the mixture as in the earlier case gave 0·32 g (60%) of **18**, m.p. 268° (Found: C, 75·76; H, 5·1; N, 13·3. Calcd for $C_{33}H_{25}N_5S$: C, 75·71; H, 4·78; N, 13·39%). The IR spectrum of **18** showed bands at 1574 and 1475 cm^{-1}, characteristic of 5-membered cyclic thioureides[21]

Thermolysis of cis-4,5-*dicarbomethoxy*-1,3,3a,6-*tetraphenyl*-4,5-*dihydropyrazolino*-[2,3-c] [1,2,3]*triazole* (**8**)

The pyrazolinotriazole **8** (0·26 g, 0·5 mmol) was heated around 200° for 30 min, under a stream of N_2 and the product mixture was chromatographed over alumina. Elution of the column with light petroleum (b.p. 60–80°) gave 0·13 g (83%) of **4**, m.p. 124° (mixture m.p.).

Thermolysis of trans-4,5-*dicarbomethoxy*-1,3,3a,6-*tetraphenyl*-4,5-*dihydropyrazolino*-[2,3-c] [1,2,3]*triazole* (**10**)

The pyrazolinotriazole **10** (0·25 g, 0·5 mmol) was heated around 200° for 15 min. Work-up of the mixture as in the earlier case, employing chromatography gave 90 mg (65%) of **4**, m.p. 124° (mixture m.p.).

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