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REACTIONS OF THE DERIVATIVES OF 5,6-DIARYL-2,5-DIHYDRO-1,2,4-TRIAZINES WITH DIMETHYL ACETYLENEDICARBOXYLATE---STRUCTURAL REASSIGNMENTS OF THE PRODUCTS AND FURTHER OBSERVATIONS

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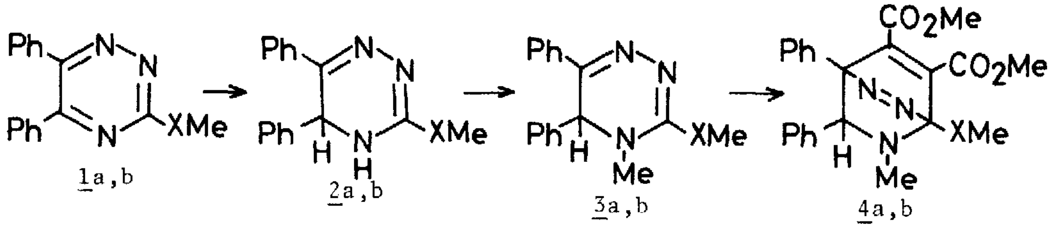
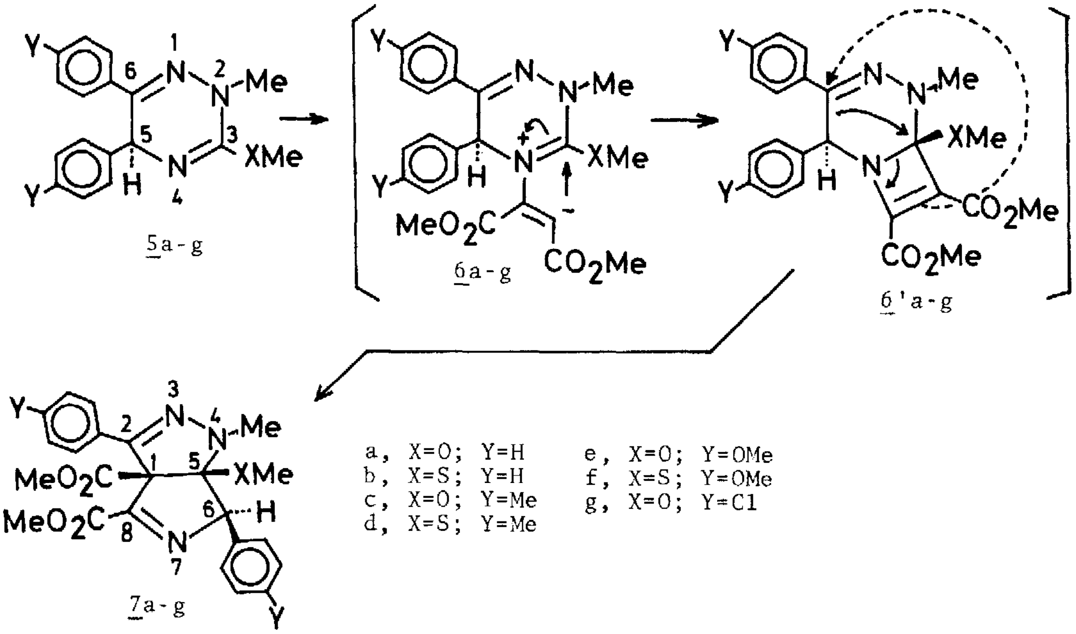
Abstract. The structures of the dihydro derivatives of 5,6-diaryl-1,2,4-triazines and of the products from the title reactions have been reassigned as 5,6-diaryl-2,5-dihydro-1,2,4-triazines (5a-g) and 2,6-diaryl-4-methyl-5-substituted-1,8-bis-methoxycarbonyl-3,4,7-triaza-bicyclo[3.3.0]octa-2,7-dienes (7a-g), respectively.

In a previous communication[1], we have assigned the structures of the dihydro derivatives of 3-methoxy- (1a) and 3-methylthio-5,6-diphenyl-1,2,4-triazine (1b) as 4,5-dihydro-1,2,4-triazines (2a-b) mainly on the basis of the fact that their mono-methylated analogs (3a-b) gave the one to one adducts (4a-b) with dimethyl acetylenedicarboxylate (DMAD). The structures of 4a-b were reasonably supported by their ^{1}HNMR-, ^{13}CNMR- and UV-spectra. Since, more recently, compounds 4a-b proved to resist thermal decomposition with nitrogen release, X-ray analysis for compound 4b as well as 3b was conducted by T. Ashida's group[2] to disclose a new synthesis of a nitrogen-containing heterocyclic system. This communication involves the correction of the structures of 3 (and hence of 2) and 4 with further observations in a series of similar synthetic reactions.

On the basis of the X-ray analyses[2], the structures of 3b and 4b have been corrected to 3-methylthio-5,6-diphenyl-2,5-dihydro-1,2,4-triazine (5b) and 2,6-diphenyl-4-methyl-5-methylthio-1,8-bis-methoxycarbonyl-3,4,7-triaza-bicyclo[3.3.0]octa-2,7-diene (7b), respectively. The skeletal identity of 5a with 5b and of 7a with 7b was firmly established in terms of chemical interrelation and spectral similarities.[1] The formation of 7a-b from 5a-b and DMAD can seemingly be explained as follows: the initially formed dipoles 6a-b[3a,4] lead to transient intermediates 6'a-b[3b], which rearrange to 7a-b as shown by the arrows, or the anionic carbon in 6 directly attacks the 6-position. At present, no deep-seated mech-



a, X=O; b, X=S



a, X=O; Y=H
b, X=S; Y=H
c, X=O; Y=Me
d, X=S; Y=Me
e, X=O; Y=OMe
f, X=S; Y=OMe
g, X=O; Y=Cl

anism for this extensive reorganization is known. That the single epimer of 7 was obtained in every reaction does not always imply the concertedness of the reaction

In order to gain a possible foothold for the mechanisms of these intriguing reactions, we chose to examine influence by para-substituents on the phenyl groups upon the reactivity of the dihydrotriazines (5) as function of electronegativity of the substituents. For this purpose, new dihydrotriazines 5c-g[6] were synthesized in like manners[7] and submitted to similar reactions with 2 equiv DMAD at 110° in toluene to give analogous products (7c-g).[8] The yields and physical constants of these products are given in Table I. The skeletal identity of these compounds are obvious from the coincidences of UV and NMR spectra of

Table I. Yields and Spectral Properties of Compounds 7a-g.

Comp. No.	Yield(%) mp(°C)	Reaction Time(hr)	λmax nm(ε)	NMR($CDCl_3$) δ
7a	65 174-176	12	215(14800,infl) 296(10400) a	C_6-H 5.49 CO_2Me 3.67,3.73 OME 3.17or3.22
7b	55 155-156	6.5	225(12100,sh) 303(11900) a	C_6-H 5.68 CO_2Me 3.67,3.78 SMe 1.87
7c	59 185.5-187.5	16	217(20700,sh) 296(17900) b	C_6-H 5.46 CO_2Me 3.71,3.75 OMe 3.18or3.21
7d	36 192-194	9	220(19200,sh) 304(13700) b	C_6-H 5.66 CO_2Me 3.70,3.87 SMe 1.87
7e	80 219-221	6	225(20200) 296(14100) b	C_6-H 5.44 CO_2Me 3.73,3.77 OMe 3.32
7f	60 200-202	12	226(20200) 303(14600) b	C_6-H 5.63 CO_2Me 3.7-3.8 SMe 1.87
7g	22 152-154	60	221(24100) 300(15100) b	C_6-H 5.47 CO_2Me 3.73 OMe 3.17or3.22

a,in MeOH. b,in 95%EtOH.

each 5-methylthio or 5-methoxy series.[9] The yields and reaction times permit, regrettably, no reasoning of the reaction mechanism. In the case of 7g, a considerable amounts of intractable side products were observed. The new triaza heterocyclic compounds (7) seem to be interesting precursors for synthesizing nitrogen-containing medium size macrocyclic rings. Further studies along this line are under way.

References and Notes

1. T. Sasaki, K. Minamoto, and K. Harada, HETEROCYCLES, 10, 93 (1978).

2. The X-ray data will be published elsewhere in near future.
3. (a) Formations of such dipolar intermediates are well documented. For example see: R. M. Acheson, "Advances in Heterocyclic Chemistry", 1, A. R. Katritzky, ed., Academic Press, 1963, p. 125.

   (b) For examples of stepwise additions of acetylenic compounds to form cyclobutenes, see: J. Bastide and O. Henri-Rousseau, "The chemistry of the carbon-carbon triple bond", Part 1, S. Patai, ed., Wiley-Intersciences, 1978, p. 447
4. That the π-electron density of 1a is largest at the 4-position has been shown by Dr. Esaki in this laboratory using the simple Hückel method. It is probably true even with the dihydrotriazine system 5. DMAD is considered to attack 4-nitrogen from less hindered side to form reasonably 6', in which 3-methoxy and 5-aryl groups in the tetrahydrotriazine ring lie in the same side of the molecule.
5. A molecular model study for the rearrangement of the presumed intermediate 6' have shown that bonding 6-carbon in the tetrahydrotriazine ring with one of the olefinic carbon atoms in the 4-membered ring requires an antara-process (dotted arrow). Thus, a σ2s + σ2s + π2a process can easily constract 7 in which the bulky phenyl group exists in the same side with 5- and 1-substituents, but this process is symmetry-forbidden.
6. The melting points and λmax (95% EtOH) of 5c-g are as follows: 5c, 73.5-75.5°, 220 (17100, infl), 234 (13800, sh), 304 (9100); 5d, 125-126°, 220 (18100, infl), 235 (14100, sh), 310 (8000); 5e, 79-81°, 223 (17700, sh), 252 (9900, sh), 284 (8900, sh), 305 (11600); 5f, 90-91.5°, 225 (21600, infl), 245 (13800, sh), 282 (8300), 312 (11900); 5g, 71-73°, 222 (18800), 240 (15500, sh), 310 (9700).
7. The skeletal identities of 5c-g with their precursors were evidenced UV-spectroscopically.
8. The reactions were usually continued until the starting material disappeared.
9. The structural similarities of 7a-g were also supported by their characteristic mass spectra.

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