HETERODIENE SYNTHESIS

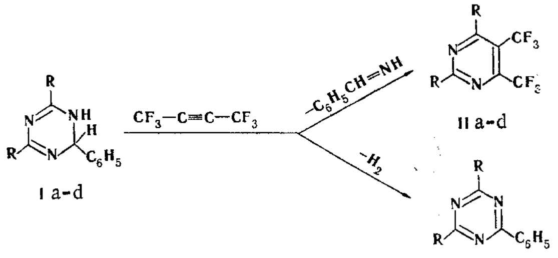
VI.* REACTION OF HEXAFLUORO-2-BUTYNE WITH 1,2-DIHYDRO-sym-TRIAZINES

N. A. Kapran, V. G. Lukamanov,
L. M. Yagupol'skii, and V. M. Cherkasov

UDC 547.853.87'221

2-Phenyl-4,6-diaryl-1,2-dihydro-sym-triazines react with hexafluoro-2-butyne as a dienophile to give 4,5-bis(trifluoromethyl)-2,6-diarylpyrimidines.

The 1,3-diaza-1,3-diene fragment in dihydro-sym-triazines reacts via the Diels–Alder scheme with diethyl acetylenedicarboxylate [2]. Hexafluoro-2-butyne reacts with 2-phenyl-4,6-diaryl-1,2-dihydro-sym-triazines (Ia-d) just like a dienophile to give 4,5-bis(trifluoromethyl)-2,6-diarylpyrimidines (IIa-d), and, in addition to this, in contrast to diethyl acetylenedicarboyxlate, it dehydrogenates Ia-c to the corresponding triazines IIIa-c, as in the dehydrogenation of dihydro-sym-triazines with tetracyanoethylene [2]. The competitive dehydrogenation is explained by the fact that the rate of 1,4-cycloaddition is low in this case. The benzaldimine liberated during the reaction was identified in the form of benzaldehyde semicarbazone.



I-III a $R=C_6H_5$; b $R=p\text{-}CH_3C_6H_4$; c $R=p\text{-}ClC_6H_4$;
d $R=p\text{-}CH_3OC_6H_4$; e $R=CCl_3$

Triazine Ie does not react like a heterodiene with hexafluoro-2-butyne and is not dehydrogenated by it, since the decrease in the electron density in the diene fragment and on the 1-N atom prevents the formation of a primary complex.

The ^{19}F NMR spectra of IIa, b are practically identical and contain two quartets at −12.05 and −25.31 ppm and − 12.04 and −25.35 ppm, respectively. The chemical shift of the high-field signal is close to the shift δ_{CF_3} in the spectrum of benzotrifluoride and is probably related to the CF_3 group in the 5 position. The signal at low field pertains to the trifluoromethyl group in the 4 position, deshielded by the adjacent nitrogen atom.

---

*See [1] for communication V.

TABLE 1. 4,5-Bis(trifluoromethyl)-2,6-diarylpyrimidines IIa-d

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	F	C	H	F	
IIa	113–114	$C_{18}H_{10}F_6N_2$	59.0	2,7	30,5	58,7	2,7	30,9	15
IIb	109–110	$C_{20}H_{14}F_6N_2$	60.9	3,2	28,4	60,6	3,6	28,7	33
IIc	94–95	$C_{18}H_8Cl_2F_6N_2$	49,3	1.8	26,1	49,4	1,8	26,1	60
IId	105–106	$C_{20}H_{14}F_6N_2O_2$	56,2	2,9	26,0	56,1	3,3	25,7	40

Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 122-123, January, 1977. Original article submitted February 13, 1976.

EXPERIMENTAL

The ^{19}F NMR spectra of acetone solutions of the compounds were obtained with a BS-487B spectrometer with trifluoroacetic acid as the external standard. The individuality of the compounds was monitored by thin-layer chromatography (TLC) on activity II Al_2O_3 in a benzene–methanol system (5 : 1) with development by iodine vapors or in UV light.

The starting 1,2-dihydro-sym-triazines (Ia-e) were obtained by the method in [1].

4,5-Bis(trifluoromethyl)-2,6-diarylpyrimidines (IIa-d, Table 1). A suspension of 10 mmole of dihydro-sym-triazine I in 30 ml of absolute benzene was heated with 13 mmole of hexafluoro-2-butyne in an autoclave at 80-90° for 30 h, after which the solvent was removed by vacuum distillation, and the residue, which began to crystallize when it was triturated with a small amount of ethanol, was removed by filtration and washed with ethanol. The filtrate was vacuum evaporated, and the residue was removed by steam distillation. The benzaldehyde was extracted from the distillate with ether and identified in the form of the semicarbazone (mp 221-222°). The solid material remaining after filtration (a mixture of II and III) was treated with acetone. Insoluble III was removed by filtration, and the II in the filtrate was crystallized from ethanol.

2,4,6-Triphenyl-sym-triazine (IIIa). This compound, with mp 228-229° [3], was obtained in 50% yield.

2-Phenyl-4,6-di(p-tolyl)-sym-triazine (IIIb). This compound, with mp 215-216° (from acetone), was obtained in 15% yield. Found: C 81.4; H 5.7; N 12.7%. $C_{23}H_{19}N_3$. Calculated: C 81.9; H 5.7; N 12.5%.

2-Phenyl-4,6-di(p-chlorophenyl)-sym-triazine (IIIc). This compound, with mp 240-241° (from benzene), was obtained in 7% yield. Found: C 66.5; H 3.5; N 11.2%. $C_{21}H_{13}Cl_2N_3$. Calculated: C 66.7; H 3.5; N 11.1%.

2-Phenyl-4,6-diaryl-sym-triazine (IIIb, c). A solution of 1 mmole of Ib, c and 1 mmole of tetrachlorobenzoquinone in 15 ml of acetone was stirred in the cold, and IIIb, c began to precipitate after a few minutes. After 3 h, the crystals were removed by filtration and washed with a small amount of acetone to give IIIb (mp 215-216°) and IIIc (mp 240-241°) in 80-90% yields (no melting-point depressions were observed for mixtures of these products with the samples indicated above).

LITERATURE CITED

1. V. M. Cherkasov and N. A. Kapran, Khim. Geterotsikl. Soedin., No. 2, 281 (1973).
2. V. M. Cherkasov, N. A. Kapran, and V. N. Zavatskii, Khim. Geterotsikl. Soedin., No. 2, 350 (1969).
3. F. W. Swamer, G. A. Reynolds, and C. R. Hauser, J. Org. Chem., 16, 43 (1951).