tion product to dimethyl sulfoxide to which an equivalent of sodium hydride had been added, followed by heating at 65° for 24 hr. and quenching with water at that temperature also gave benzophenone, 80%.

Reaction of Benzophenone and Dimethyl Sulfoxide.—Equivalent quantities of potassium *t*-butoxide (or sodium hydride) and benzophenone were added to dimethyl sulfoxide in a dry box to give an approximately 0.5 *M* solution which was stirred under nitrogen at 70–80°. The reaction mixture (or an aliquot) was cooled and poured into water, and the resulting mixture extracted with carbon disulfide or methylene chloride, the extract dried, and solvent removed. The residue was examined by g.l.c., either directly or after a preliminary vacuum distillation, using an Aerograph Model A 350 instrument and silicone column programmed at 160–240°, 6°/min. with biphenyl as an internal standard. Products were identified as follows.

Diphenylmethane, 1,1-Diphenylethylene.—Products obtained by collection of g.l.c. peaks had retention times, infrared spectra and n.m.r. spectra identical with authentic samples.

1,1-Diphenylcyclopropane.—The product obtained by collection of the appropriate g.l.c. peak showed an infrared spectrum consistent with the indicated structure, and a two-peak n.m.r. spectra, $\tau = 2.95$ (aromatic) and $\tau = 8.76$ (methylene) relative areas 5:2.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.73%; H, 7.36%. Found: C, 92.46%; H, 7.36%.

Reaction of 1,1-Diphenylethylene with Dimethyl Sulfoxide.—The reaction was carried out in the same manner as those involving benzophenone. After heating for 18 hr. at 80°, the mixture was quenched with water, extracted, the solvent removed, and the residue vacuum distilled. G.l.c. analysis showed diphenylmethane (17%) and 1,1-diphenylcyclopropane (6%), identified as above, together with another major peak (77%) of longer retention time. This was collected and identified as 3,3-diphenylpropene, on the basis of infrared, ultraviolet, and n.m.r. spectra and analysis. Infrared and ultraviolet spectra were those expected for two phenyl groups and an unconjugated $—CH{=}CH_2$. The n.m.r. spectra showed three peaks (relative areas 10:1:3, respectively), 3.06, (singlet, aromatic H); 3.9 (broad multiplet $—CH{=}$); and 5.26 (unsymetric multiplet $Ph_2CH—$ plus $=CH_2$).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.73%, H, 7.36%. Found: C, 92.97%, H, 7.31%.

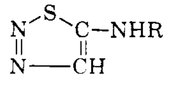
Synthesis and Absorption Spectra of 5-(Substituted) Amino-1,2,3-thiadiazoles[1]

Eugene Lieber,[2] N. Calvanico, and C. N. R. Rao[3]

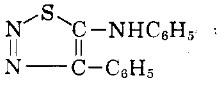
Departments of Chemistry, Roosevelt University and DePaul University, Chicago, Illinois

Received August 15, 1961

A series of 5-(substituted) amino-1,2,3-thiadiazoles (I) have been prepared by the reaction of diazomethane with organic isothiocyanates, first discovered by Pechmann[4,5] and later examined by Sheehan.[6] Its extension



I



II

to diazo derivatives other than diazomethane has not been studied. A further limitation of the reaction is the inertness of diazomethane to methyl isothiocyanate. This paper reports on the synthesis of eight new compounds of type I (Table I) as well as the successful condensation of phenyldiazomethane with phenyl isothiocyanate to form 4-phenyl-5-anilino-1,2,3-thiadiazole (II). The infrared and ultraviolet absorption spectral data for these compounds have also been studied. (See p. 258 for Tables I, II, and III.)

The ultraviolet absorption data (Table II) in I clearly show that the thiadiazole ring is aromatic in nature. Comparison of the spectra of I with those of 5-(substituted phenyl)amino-1,2,3,4-thiatriazoles[7] indicates that the thiadiazole ring is less electronegative than the thiatriazole ring. This is understandable since in the later heterocycle a nitrogen atom replaces a carbon of the thiadiazole system. It has been similarly found that the tetrazole ring is more electronegative than the triazole ring.[8]

The major characteristic infrared frequencies of the 5-(substituted phenyl)amino-1,2,3-thiadiazoles are listed in Table III with the appropriate assignments. The assignments were made following the recent review on the infrared spectra of heterocyclic systems by Katritsky.[9] It is not possible to assign frequencies to the N=N and C=C of the thiadiazole ring since it is a conjugate system.

Experimental[10]

The mode of synthesis is essentially that described by Sheehan.[5] The results are summarized in Table I. With two exceptions, noted in Table I, the product precipitates on refrigeration over periods from 1 to 3 days. Where precipitation of product did not occur the ether was removed and the residue recrystallized or precipitated by means of another solvent. The typical procedure is illustrated for one of the new compounds and for II.

5-Benzylamino-1,2,3-thiadiazole (I. R = $C_6H_5CH_2$).—To a solution of 15 g. (0.10 mole) of benzyl isothiocyanate was added 0.2 mole of a cold etheral solution of diazomethane.[11] The solution was refrigerated overnight and the ether evaporated to dryness. Yellow needles weighing 1.4 g. (7.3%) were obtained. The analytical sample was recrystallized from absolute ethanol yielding white needles, m.p. 93–95°.

5-(*p*-Nitrophenylamino)-1,2,3-thiadizole (I. R = 4-$O_2NC_6H_5$).—A tan powder results on the reaction of *p*-nitrophenyl isothiocyanate and diazomethane in cold ether. Many attempts were made in numerous solvents to obtain an analytically pure specimen. The evidence shows it to be the least stable type I and that it is obtained in its highest state of purity on initial precipitation from the reaction mixture.

4-Phenyl-5-anilino-1,2,3-thiadiazole (II).—To a solution of phenyl isothiocyanate (0.008 mole, 1.1 g.) in 10 ml. of dry ether was added 40 ml. (0.008 mole) of phenyldiazomethane in ether[12] and the mixture allowed to refrigerate overnight. The ether was removed by evaporation and the liquid residue was boiled in 50 ml. of dry ethanol. On cooling a yellow powder is precipitated (in some trials a portion of the ethanol must be removed before precipitation can be induced), yielding 1.1 g. (53%) which melted to a viscous liquid at 80–83°.

Anal. Calcd. for $C_{14}H_{11}N_3S$: N, 16.72; S, 12.67. Found N, 16.48; S, 13.18.

---

[1] The authors gratefully acknowledge the support of these studies by the U. S. Army Research Office.

[2] To whom all correspondence should be addressed.

[3] Present address, Indian Institute of Science, Bangalore, India.

[4] H. V. Pechmann and A. Nold, *Ber.*, **29**, 2588 (1896).

[5] H. V. Pechmann, *ibid.*, **28**, 861 (1895).

[6] J. C. Sheehan and R. T. Izzo, *J. Am. Chem. Soc.*, **71**, 4059 (1949).

[7] E. Lieber, J. Ramachandran, C. N. R. Rao, and C. N. Pillai, *Can. J. Chem.*, **37**, 563 (1959).

[8] E. Lieber, C. N. R. Rao, T. S. Chao, and J. Ramachandran, *J. Org. Chem.*, **23**, 1916 (1959).

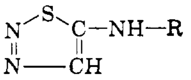
[9] A. R. Katritzky, *Quart. Rev.*, **4**, 353 (1959).

[10] Analyses were done by Drs. G. W. Weiler and F. B. Strauss, Oxford, England. Melting points (Fisher block) are uncorrected. The infrared spectra were obtained with the Perkin-Elmer 21-C infrared spectrophotometer with sodium chloride optics. The ultraviolet spectra were obtained in purified dioxane (0.05 mg./ml.) on a Beckman DU spectrophotometer. The wave lengths throughout are expressed in millimicrons and the intensities of absorption in terms of the logarithm of the molar extinction coefficients.

[11] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1951.

[12] P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958).

TABLE I. 5-(Substituted) Amino-1,2,3-thiadiazoles

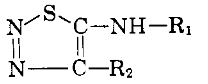


R^a	Yield, %^{d}	Crystalline^e form	M.p., °C.^{g}	Formula	N Calcd.	N Found	S Calcd.	S Found
C_6H_5	42.0	Grey needles	180	$C_8H_7N_3S$	23.71	23.80	18.09	17.80
$C_6H_5CH_2$^{b}	7.3	White needles	93–95	$C_9H_9N_3S$	22.19	22.21	16.75	16.52
4-$O_2NC_6H_4$	20.0	Tan powder	206–209	$C_5H_6N_4SO_2$	25.18	23.80	14.42	13.80
4-$CH_3OC_6H_4$	10.0	Colorless flakes^f	155–157	$C_9H_9N_3SO$	20.30	20.40	15.48	15.10
4-ClC_6H_4	10.0	Tan powder	173–175	$C_8H_6N_3SCl$^{h}	19.85	19.60	15.17	15.71
4-BrC_6H_4	13.0	Brown flakes	187–189	$C_8H_6N_3SBr$^{i}	16.40	16.15	12.50	12.77
4-$CH_3C_6H_4$	35.5	Yellow needles	172–174	$C_9H_9N_3S$	22.19	22.40	16.75	16.38
4-$(CH_3)_2NC_6H_4$^{c}	23.0	Green powder	168–170	$C_{10}H_{12}N_4S$	25.42	24.60	14.53	14.00
$C_{10}H_7$^{k}	20.0	Yellow needles	161–162	$C_{12}H_9N_3S$	18.50	18.35	13.55	14.26
3-BrC_6H_4	37.0	Tan scales	165–166	$C_8H_6N_3SBr$^{j}	16.40	16.80	12.50	12.85

[a] All are new compounds with exception of R = C_6H_5 (lit.,[5] m.p. 179–180°). [b] Product did not precipitate; ether was removed and residue recrystallized. [c] Product did not precipitate; ether was removed and product precipitated by benzene. [d] Represent first crop of crystals. [e] From ethanol. [f] From chloroform. [g] With decomposition except R = $C_6H_5CH_2$. [h] Cl: calcd., 16.78; found, 16.90. [i] Br: calcd., 31.17; found, 31.15. [j] Br: calcd., 31.17; found, 31.40. [k] α-Naphthyl.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF 5-(SUBSTITUTED) AMINO-1,2,3-THIADIAZOLES



R_1	R_2	λ_{max}	Log ϵ_{max}	λ_{max}	Log ϵ_{max}	λ_{max}	Log ϵ_{max}
$C_6H_5CH_2$	H	240	4.54	266	4.48	296	4.53
3-Br—C_6H_4	H	246	4.21			314	4.34
						324	4.36
4-Cl—C_6H_4	H	258	3.94			310	4.26
						330	3.97
4-CH_3—C_6H_4	H	246	3.90			324	4.21
α-Naphthyl	H	232	4.47	236	4.27	334	4.21
				240	4.28		
$C_6H_5^-$	C_6H_5	236	4.05	242	3.89	316	3.49
				254	3.84		
				274	3.71		
$C_6H_5^-$	H	240	3.96	280	3.66	318	4.05
4-$CH_3OC_6H_4$	H	230	4.06			320	3.77
		240	4.03				
4-BrC_6H_4	H	252	3.93			320	4.24
4-$(CH_3)_2NC_6H_4$	H	260	4.34			324	4.17

TABLE III

MAJOR CHARACTERISTIC INFRARED FREQUENCIES OF 5-(SUBSTITUTED) AMINO-1,2,3-THIADIAZOLES

Cm.$^{-1a}$	Assignment
3220 m	Bonded N—H stretching
1650–1590 v	N—H deformation
1560–1475 v^b	Ring stretching
1350–1280 v^d	C—N stretching
1265–1200 v	C—H in-plane deformation
1190–1175 v^d	C—H in-plane deformation
1150–950 v^d	Ring breathing
910–890 w	Ring breathing
705–670 w	C—H out-of-plane deformation

[a] Intensity: m, medium; w, weak; v, variable. [b] One or more bands. [c] Two bands. [d] At least one band.

Some Reactions of Fluorinated Cyclobutenes with Grignard Reagents

J. D. PARK AND R. FONTANELLI[1]

Department of Chemistry, University of Colorado, Boulder, Colorado

Received April 20, 1962

In an attempt to find a simple method for introducing alkyl and aryl substituents into fluorocyclobutenes, our attention was turned to the reaction of Grignard reagents with these compounds. This had not been carried out previously.

The reaction of Grignard reagents with fluoroölefins, such as $CF_2{=}CCl_2$, $CF_2{=}CFCl$, and $CF_2Cl{-}CF{=}CF_2$, has already been described by Tarrant, *et al.*[2] These workers found that apparently addition first occurs across the double bond and the resulting adduct loses MgX_2 to give a new, longer chain fluoroölefin. The reaction goes with poor yield (10–20%) using aliphatic Grignard reagents and with better yields (30–70%) using aromatic Grignard reagents.

The preparation of some alkyl derivatives (mono- and dimethyl, mono- and dibutyl, and diphenyl) of perfluorocyclobutene, has been previously described by Dixon,[3] using the reaction with alkyllithium. This reaction, however, gives in poor yields (20–40%) only the diphenyl derivative with phenyllithium and a mixture of mono- and dialkyl derivatives (the latter predominating) with alkyllithium.

In this study, when the perfluorocyclobutene was treated with excess alkylmagnesium bromide under mild conditions, the monoalkyl derivatives in high yields (75–85%) (methyl excepted) had been obtained. Under stronger conditions, the monoalkyl derivatives with excess Grignard reagent gave comparable yields of the dialkyl derivatives. However, the reaction with phenylmagnesium bromide gave both the mono- and diphenyl derivatives (ratio 1:1) in a total yield of 80%.

Some reactions with vinyl- and perfluoroalkylmagnesium bromide have been attempted, but only high boiling polymeric materials were isolated.

When 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene was treated with alkyl Grignards, the substitution of one vinylic chlorine took place quite readily. The substitution of the second vinylic chlorine, on the contrary, does not easily take place, even after refluxing the monoalkyl derivative for twenty-four hours in ether. This reaction has been carried out in a sealed Pyrex tube in ether under autogenous pressure, and only above 100° a reaction took place. The reaction products isolated were: starting material (25%), 1,2-diethyl-3,3,4,4-tetrafluorocyclobutene (16%) (this product was identical

---

[1] Montecatini Industrial Research Fellow (1961–1962). Work done at the University of Colorado.

[2] P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).

[3] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).