9 fractions was collected. The oil from the second fraction when washed with ethanol gave a white solid which was crystallized from ethyl acetate to give 0.15 g. of tetraphenylsilane, identified by means of a mixed melting point with an authentic sample. Removal of the solvent from the third fraction left a yellow paste which was refluxed in petroleum ether. There was isolated 1.4 g. (13%) of product melting at 149–152°. Two additional crystallizations gave an analytical sample of 2-chloro-2′-(triphenylsilyl)-biphenyl melting at 157.5–158.5°.

Anal. Calcd. for $C_{30}H_{23}ClSi$: Si, 6.28. Found: Si, 6.23, 6.27.

Fraction four gave 0.25 g. of pale yellow plates melting at 194–196°. A mixed melting point with an authentic sample of triphenylene showed no depression.

2-Bromo-2′-(triphenylsilyl)-biphenyl.—A solution of 25 ml. (0.032 mole) of butyllithium was added over a period of 6 min. to a rapidly stirred solution of 10 g. (0.032 mole) of 2,2′-dibromobiphenyl in 100 ml. of dry ether. A temperature of −20° was maintained during the addition. After completing the addition, the mixture was stirred at −15° for 45 min. Subsequently 9.44 g. (0.032 mole) of triphenylchlorosilane dissolved in 85 ml. of ether was added at −15°, and the mixture was allowed to warm to room temperature. The mixture was stirred overnight at room temperature and then was refluxed for 7 hr. after which time Color Test I was positive. After adding 100 ml. of *n*-heptane, the resulting mixture was distilled until an internal temperature of 70° was reached, whereupon a negative color test was obtained after 20 min. The mixture was hydrolyzed with water. An insoluble material was filtered and crystallized from ethanol to give colorless needles, 1.92 g., m.p. 152–153°. Work-up of the filtrate as described in the preceding experiment yielded an additional 1.81 g. of product, m.p. 147–149°. The total yield of 2-bromo-2′-(triphenylsilyl)-biphenyl was 3.73 g. (24%). The analytical sample melted at 152.5–154°.

Anal. Calcd. for $C_{30}H_{23}BrSi$: Si, 5.71. Found: Si, 5.63, 5.45.

The infrared spectrum of the bromo-isomer as a carbon disulfide solution was very similar to that of the chloro-isomer, thus indirectly confirming the structure of the latter.

Acknowledgments.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio, for financial assistance. They also are grateful to the Institute for Atomic Research, Iowa State College, and Mr. E. Miller Layton for assistance in the infrared determinations.

AMES, IOWA

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Reactions of Trichloromethyl-1,3,5-triazine Derivatives with Amines[1]

BY ALFRED KREUTZBERGER

RECEIVED SEPTEMBER 19, 1956

A method has been found which, by means of amines, permits the replacement by NHR-groups of all trichloromethyl groups attached to a 1,3,5-triazine ring. Use of diamines leads to longer chains of higher molecular 1,3,5-triazine compounds. In 1,3,5-triazine derivatives bearing both trichloromethyl and carbethoxy groupings, ammonia reacts first of all with one trichloromethyl group.

As is well known, the trichloromethyl groups of several organic compounds like chloral, trichloroacetic acid, trichloroacetone and others are split off upon reaction with alkali to form anions[2] which then, by combining with a proton, form chloroform. In connection with investigations on trichloromethyl-1,3,5-triazines,[3,4] especially 2-methyl-4,6-bis-trichloromethyl-1,3,5-triazine (I) and 2-phenyl-4,6-bis-trichloromethyl-1,3,5-triazine (II),[5] it was desirable to know whether these compounds reacted with bases analogously. The various replacement reactions of trichloromethyl groups attached to the 1,3,5-triazine ring by NHR-groups are described in the present article, along with some comparable observations on carbethoxytrichloro-1,3,5-triazines.

In the reaction of I or II with concentrated aqueous ammonia, only one of the two trichloromethyl groups turned out to be replaceable by the NH_2-group under very mild conditions, thus yielding 2-methyl-4-amino-6-trichloromethyl-1,3,5-triazine (III) and 2-phenyl-4-amino-6-trichloromethyl-1,3,5-triazine (IV), respectively. An attempt to replace the last trichloromethyl group by increasing the reaction temperature failed. Instead, at higher temperatures compound I yielded quantitatively 2-methyl-4-amino-6-hydroxy-1,3,5-triazine (V) upon reaction with aqueous ammonia and a mixture of III and V upon reaction with ethanolic ammonia solution.[6]

It was, however, desired to find a method by which all trichloromethyl groups attached to a triazine ring could be replaced by NHR-groups, because application of diamines would then lead to higher molecular compounds containing two or more 1,3,5-triazine rings linearly connected. This objective was achieved through working in OH-free media, like dioxane, chloroform and N,N-dimethylformamide.

Thus, by bubbling ammonia into a solution of I in N,N-dimethylformamide, 2-methyl-4,6-diamino-1,3,5-triazine (XI) was obtained. By the same

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[1] This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, Baltimore, Md.

[2] F. Arndt and B. Eistert, *Ber.*, **68**, 196 (1935).

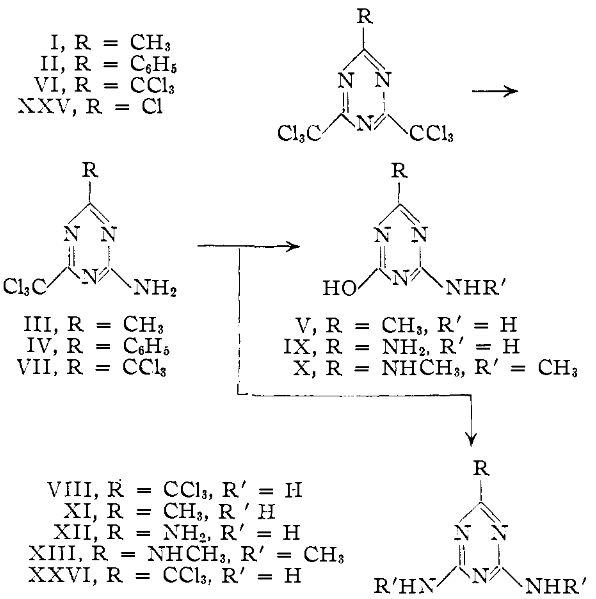
[3] Ch. Grundmann and G. Weisse, *Chem. Ber.*, **84**, 684 (1951).

[4] Ch. Grundmann, H. Ulrich and A. Kreutzberger, *ibid.*, **86**, 181 (1953).

[5] K. Dachlauer, German Patent 682,391, Oct., 1939 (to I. G. Farbenindustrie A.-G.).

[6] These findings are in conformity with the results obtained from the action of concd. aqueous ammonia on 2,4,6-tris-trichloromethyl-1,3,5-triazine (VI) as reported by A. Weddige, *J. prakt. Chem.*, [2] **33**, 81 (1886). Only the first two trichloromethyl groups in VI could be replaced by the amino group with formation of 2-amino-4,6-bis-trichloromethyl-1,3,5-triazine (VII) and 2,4-diamino-6-trichloromethyl-1,3,5-triazine (VIII). Similar results were obtained when methylamine was used in place of concd. aqueous ammonia. The substitution by the NHR-group of the last trichloromethyl group in VI, however, could not even be forced under more severe conditions, and as end product only 2,4-diamino-6-hydroxy-1,3,5-triazine (IX) and 2,4-bis-methylamino-6-hydroxy-1,3,5-triazine (X), respectively, could be obtained.

procedure, the conversion of VI with ammonia into 2,4,6-triamino-1,3,5-triazine (XII) and with methylamine into 2,4,6-tris-methylamino-1,3,5-triazine (XIII) was successful.



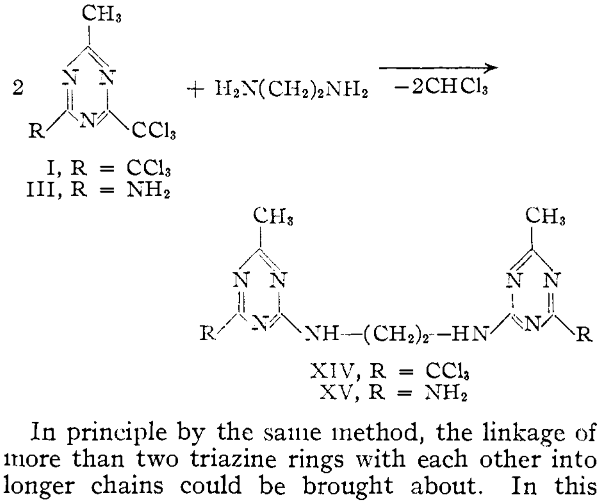
I, R = CH_3
II, R = C_6H_5
VI, R = CCl_3
XXV, R = Cl

III, R = CH_3
IV, R = C_6H_5
VII, R = CCl_3

V, R = CH_3, R′ = H
IX, R = NH_2, R′ = H
X, R = $NHCH_3$, R′ = CH_3

VIII, R = CCl_3, R′ = H
XI, R = CH_3, R′ H
XII, R = NH_2, R′ = H
XIII, R = $NHCH_3$, R′ = CH_3
XXVI, R = CCl_3, R′ = H

Furthermore, by the above procedure but using diamines, the linkage of two triazine rings was achieved. Thus the reaction of two molecules of I with one molecule of ethylenediamine in chloroform led to N,N′-bis-[2-methyl-4-trichloromethyl-1,3,5-triazinyl-(6)]-ethylenediamine (XIV). In addition, by the above method, the reaction of the last trichloromethyl group of the triazine ring with diamine could be brought about. Two molecules of III on reaction with one molecule of ethylenediamine in dioxane yielded N,N′-bis-[2-methyl-4-amino-1,3,5-triazinyl-(6)]-ethylenediamine (XV).

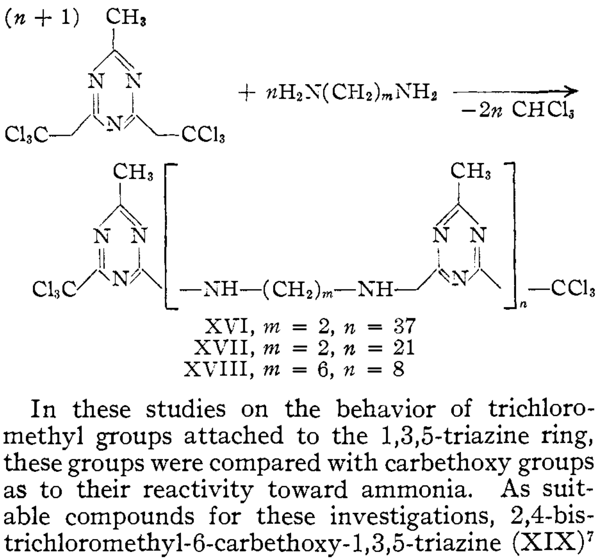


I, R = CCl_3
III, R = NH_2

XIV, R = CCl_3
XV, R = NH_2

In principle by the same method, the linkage of more than two triazine rings with each other into longer chains could be brought about. In this case the molar ratio between I and the diamine had to be about 1:1 and a longer reacting time had to be allowed. At first, for the purpose of the determination of the molecular weight of these polymers, some measurements of specific viscosity were made which showed, upon comparison with the analytically found chlorine values, that the chain ends of the polymers consisted of trichloromethyl groups. That, in turn, meant that in subsequent experiments the molecular weight could be calculated simply from the analytical chlorine values. The accuracy of the chlorine analyses limits the accuracy of the calculation of the n-values for formulas XVI and XVII to ±3.

Generally the chain length proved to be essentially dependent on the kind of diamine and the solvent used. Thus the reaction of I with ethylenediamine in m-cresol yielded a polymer XVI having a molecular weight of 5920, while the same starting materials in N,N-dimethylformamide gave the polymer XVII with a molecular weight of 3500. Using the latter solvent for the reaction between I and hexamethylenediamine, the polymer XVIII with the somewhat lower molecular weight of 1990 was obtained. All these polymers, particularly XVIII, exhibit molding properties in the molten state.



XVI, $m = 2$, $n = 37$
XVII, $m = 2$, $n = 21$
XVIII, $m = 6$, $n = 8$

In these studies on the behavior of trichloromethyl groups attached to the 1,3,5-triazine ring, these groups were compared with carbethoxy groups as to their reactivity toward ammonia. As suitable compounds for these investigations, 2,4-bis-trichloromethyl-6-carbethoxy-1,3,5-triazine (XIX)[7] and 2-trichloromethyl-4,6-bis-carbethoxy-1,3,5-triazine (XX)[7] were chosen. Subjecting these two compounds to conditions under which in the aforementioned cases only one CCl_3 group was replaced by an NH_2 group, not only one CCl_3 group, but also one (in XIX) or two (in XX) carbethoxy groups reacted. Thus XIX was converted to 2-amino-4-trichloromethyl-6-carbamyl-1,3,5-triazine (XXI). The reaction product of XX was assigned the constitution of 2-hydroxy-4,6-bis-carbamyl-1,3,5-triazine (XXII) on the basis of the fact that it is insoluble in $NaHCO_3$, Na_2CO_3 and diluted NaOH solutions, but soluble in concd. NaOH solution. Thus, the question as to whether the CCl_3 group in XX acts toward ammonia as a "first" or "last" CCl_3 group, is to be answered in favor of the latter possibility on account of the OH-substitution.

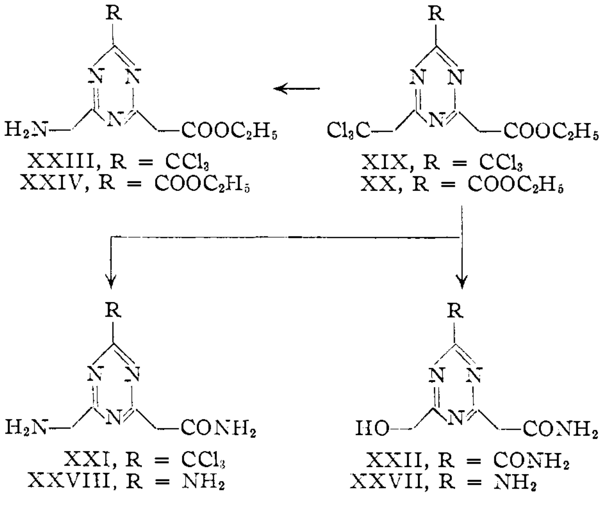
Since under these conditions the two different functional groups of both XIX and XX reacted simultaneously, no conclusions as to their relative reactivities could be drawn. Thus milder conditions of reaction seemed indicated. It was found that when exactly equimolar amounts of ammonia and the triazine derivative were caused to react in absolute ethereal solution at 0°, only one functional

[7] Ch. Grundmann, G. Weisse and S. Seide, *Ann.*, **577**, 81 (1952).

group, *viz.*, the CCl_3 group, was replaced. Thus, XIX furnished 2-amino-4-carbethoxy-6-trichloromethyl-1,3,5-triazine (XXIII) while XX yielded 2-amino-4,6-bis-carbethoxy-1,3,5-triazine (XXIV). Summarizing, it can be said that in 1,3,5-triazine derivatives containing both CCl_3 and $COOC_2H_5$ groups, the first CCl_3 is the most reactive of these functional groups toward ammonia. Second in order of activity, however, is not the second CCl_3 group but the $COOC_2H_5$ group as is evidenced by the formation of XXI.

In this connection it may be worthwhile to notice that when both CCl_3 and Cl groups are attached to the 1,3,5-triazine nucleus, the first CCl_3 group reacts most easily with ammonia. Thus 2,4-bis-trichloromethyl-6-chloro-1,3,5-triazine (XXV) reacts with ammonia to give 2-trichloromethyl-4,6-diamino-1,3,5-triazine (XXVI).[8] In this reaction no formation of the intermediate 2,4-bis-trichloromethyl-6-amino-1,3,5-triazine, which is stable under the conditions employed, was observed.

In analogy with the formation of V, the action of concentrated aqueous ammonia on XIX or XXI at elevated temperatures yielded 2-amino-4-hydroxy-6-carbamyl-1,3,5-triazine (XXVII), thus replacing the last CCl_3 group by a hydroxy rather than by an amino group. In this reaction, in addition to XXVII, only minor amounts of 2,4-diamino-6-carbamyl-1,3,5-triazine (XXVIII) were obtained. As in preceding cases, the replacement of the last CCl_3 group in XXI by NH_2 was attained by means of gaseous ammonia and N,N-dimethylformamide as solvent. In this manner, XXVIII was the sole reaction product.



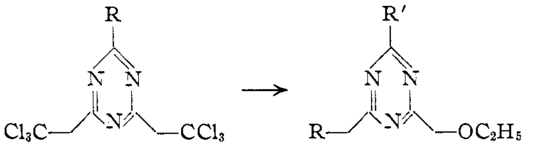
XXIII, R = CCl_3
XXIV, R = $COOC_2H_5$

XIX, R = CCl_3
XX, R = $COOC_2H_5$

XXI, R = CCl_3
XXVIII, R = NH_2

XXII, R = $CONH_2$
XXVII, R = NH_2

As may be expected, the nucleophilic replacement of the CCl_3 group attached to the 1,3,5-triazine ring also proceeds with other suitable agents, *e.g.*, ethanol. The latter, upon reaction with trichloromethyl-1,3,5-triazine derivatives, gives principally the analogous results as ammonia. The only difference appears to be one of degree in that ethanol reacts more powerfully. Thus VI reacts with ethanol in the presence of a base to give directly 2,4,6-tris-ethoxy-1,3,5-triazine (XXIX), intermediates analogous to VII and VIII not being isolable.[9] XXIX also was obtained by the action of ethanol on XXV in the presence of sodium ethoxide, in this case the expected intermediates being isolable.[10] Another case of nucleophilic substitution of the CCl_3 group in the 1,3,5-triazine series was observed when it was attempted to dehalogenate XIX by hydrogen using ethanol as solvent, palladium-on-charcoal as catalyst and triethylamine as scavenger to bind HCl. In this reaction 2-ethoxy-4-methyl-6-carbethoxy-1,3,5-triazine (XXX) was obtained as one of the products.[11]



VI, R = CCl_3
XIX, R = $COOC_2H_5$
XXV, R = Cl

XXIX, R = R′ = OC_2H_5
XXX, R = CH_3, R′ = $COOC_2H_5$

Acknowledgment.—The author is very much indebted to the Olin Mathieson Chemical Corporation for their generous support of this work. Furthermore he wishes to thank Dr. C. J. Grundmann of this Laboratory for his interest in the work and for stimulating discussions.

Experimental[12]

General Procedure Used for the Reaction of Trichloromethyl-1,3,5-triazine Derivatives. (A) With Concentrated Aqueous Ammonia (28%) at Room Temperature.—A suspension of 5 to 10 g. of the particular trichloromethyl-1,3,5-triazine derivative in 20 to 40 ml. of 28% aqueous ammonia was shaken for 2 to 3 hr. at room temperature, with an additional 15 to 25 ml. of the aqueous ammonia being added from time to time in smaller portions. Chloroform was evolved thereby. In some cases also heat was evolved so that cooling was necessary to maintain the suspension at room temperature. In other cases a somewhat elevated temperature (up to 50°) was necessary. The reaction product was vacuum-filtered, dried and recrystallized. Compounds III, IV, XXI and XXII in Table I were prepared by this procedure.

(B) With Aqueous Ammonia (28%) at 100°.—Batches of the type and size described under (A) were heated on a water-bath for 4 hr. Thereafter they were evaporated to dryness and the residues were recrystallized. Compounds V, IX and XXVII were produced by this procedure.

(C) With Amines in OH-free Solvents.—An amount of 5 to 10 g. of the requisite trichloromethyl-1,3,5-triazine derivative was, respectively, dissolved or suspended in N,N-dimethylformamide, chloroform or dioxane. If the amine was gaseous, it was bubbled into the reaction mixture, the temperature varying between room temperature and 165° according to the ease of the reaction. The liquid amines were added to the reaction mixture which was then shaken at a temperature chosen as explained above. The end-point of the reaction was evidenced by cessation of chloroform evolution and was usually reached after a total reaction time of 2 to 4 hours. If the reaction product remained in solution, the reaction mixture was evaporated to dryness, but if the reaction product precipitated, it was vacuum-filtered and dried. The solids were then either recrystallized or, if a suitable solvent could not be found, they were purified by extracting the impurities with ethanol, acetone and ether. Examples are listed in Table I as XI, XII, XIII, XIV, XV and XXVIII.

Polymer XVI.—Ethylenediamine (2.0 g.) was added to a solution of I (10.0 g.) in *m*-cresol (25.0 g.) and the mixture heated for 4 hr. at 205–210°. From the resulting reddish brown oil the solvent was distilled off *in vacuo* and the crude

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(8) H. Schroeder and Ch. Grundmann, THIS JOURNAL, **78**, 2447 (1956).

(9) Ch. Grundmann and E. Kober, unpublished results.

(10) H. Schroeder and Ch. Grundmann, unpublished results.

(11) Ch. Grundmann and G. Weisse, unpublished results.

(12) All melting points are corrected.

TABLE I

SUBSTITUTION OF CCl_3 GROUPS ATTACHED TO A 1,3,5-TRIAZINE RING

Starting compound	Amine	Solvent	Temp., °C.	Reacn. time, hr.	Resulting compound	Yield, %	Recrystn. solvent	Solubility	M.p., °C. cor.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
I	NH_3	Water[a]	25	2	III	79	Methanol–H_2O 55:45	Ins. petr. ether, sl. sol. CS_2, sol. Y[b]	158–159	$C_5H_5N_4Cl_3$	26.40	26.38	2.22	2.43			46.8	46.8
II	NH_3	Water	40–50	2	IV	90	Acetone–H_2O 1:1	Ins. water, petr. ether; sl. sol. CS_2; sol. Y[b]	175–176	$C_{10}H_7N_4Cl_3$					19.35	19.47	36.73	36.65
I	NH_3	Water	100	4	V	100	Water	Ins. benzene, sol. water	>400	$C_4H_6N_4O$	38.10	37.84	4.80	4.86	44.43	44.52		
I	NH_3	DMF[c]	165	3.5	XI	51	Water	Sol. water, ethanol	278–279	$C_4H_7N_5$	Ident. by mixed m.p. with authentic sample[d]							
VI	NH_3	DMF	165	4	XII	48	Water	Sol. water, insol. Z[e]		$C_3H_6N_6$	Identification as picrate[f]							
VI	CH_3NH_2	DMF	165	2.5	XIII	44	Water	Sol. water, ethanol	115	$C_6H_{12}N_6$	Ident. by mixed m.p. with authentic sample[g]							
I	$CH_2(NH_2)_2$	$CHCl_3$	25	2	XIV	14	Ethanol–H_2O 7:3	Ins. water, sl. sol. ether, sol. Y[b]	221–222	$C_{12}H_{12}N_8Cl_6$					23.29	22.89	44.23	44.01
III	$CH_2(NH_2)_2$	Dioxane	130	2	XV	42		Ins. water and Z[e]	328–330	$C_{10}H_{16}N_{10}$	43.46	43.43	5.84	6.11				
XIX	NH_3	Water	25	3	XXI	80	Gl. HAc	Sol. pyridine, nitrobenzene, gl. acetic acid, ethyl malonate	315–316	$C_5H_4Cl_3N_5O$	23.41	23.21	1.57	1.75				
XX	NH_3	Water	25	2	XXII	89		Ins. water and Z[e]	>400	$C_5H_5N_5O_3$	32.79	32.72	2.75	2.62	38.25	38.41		
XIX	NH_3	DMF	25	3.5	XXVIII	100	Water	Sol. water, glacial acetic acid, tetrahydrofurfuryl alcohol; ins. Y[b]	>400	$C_4H_6N_6O$	31.16	31.08	3.92	4.20	54.53	54.50		

[a] With ethanol as solvent at 100°, a mixture of III and V was obtained; yields: 58% of III and 13% of V. [b] Y = all other common organic solvents. [c] DMF = N,N-dimethylformamide. [d] M. Nencki, *Ber.*, **7**, 776 (1874). [e] Z = all common organic solvents. [f] A. Werner, *J. Chem. Soc.*, 107, 721 (1915). [g] A. W. Hofmann, *Ber.*, 18, 2763 (1885).

brown remainder best purified by successive boiling out with alcohol and acetone. Thus a faintly yellow powder was obtained which was insoluble in all usual organic solvents; m.p. about 370°, yield 3.0 g. (64%).

Anal. Calcd. for $C_{228}H_{336}N_{188}Cl_6$: C, 46.24; H, 5.72; Cl, 3.59. Found: C, 46.56; H, 5.79; Cl, 3.59, 3.58.

Polymer XVII.—Ten parts by weight of I and two parts by weight of ethylenediamine were dissolved in 25 parts by weight of N,N-dimethylformamide and heated for 3 hr. at 170–180°, thereby precipitating a yellowish brown mass, the amount of which could be increased by adding acetone to the cooled suspension. Since the product obtained could not be recrystallized, the best way to purify it was by separate extractions with boiling acetone and alcohol. The yellowish powder so obtained amounted to 3.5 g. (73%) and melted at about 250°.

Anal. Calcd. for $C_{132}H_{192}N_{108}Cl_6$: C, 45.25; H, 5.52; Cl, 6.07. Found: C, 45.23; H, 5.97; Cl, 6.06, 6.21.

Polymer XVIII.—A mixture of 10.0 g. of I, 3.5 g. of hexamethylenediamine and 25 ml. of N,N-dimethylformamide was heated for 3 hr. at 160–170°. During this time the crude condensation product precipitated. After cooling, the reaction mixture was diluted with acetone, boiled for a short time and filtered. Since the solid was insoluble in lower boiling solvents like carbon tetrachloride or acetone and soluble in higher boiling ones like nitrobenzene but could not, however, be recrystallized from the latter ones, it could be purified best by successive extractions with boiling acetone, alcohol and carbon tetrachloride. The yellow powder so obtained melted at 200–201°, yield 2.5 g. (37%). Soluble also in mineral acids, XVIII could be reprecipitated from such a solution by neutralization with dilute alkali.

Anal. Calcd. for $C_{86}H_{139}N_{43}Cl_6$: C, 51.93; H, 7.05; Cl, 10.69. Found: C, 51.96, 51.76; H, 7.34, 7.42; Cl, 10.42, 10.40.

2-Amino-4-carbethoxy-6-trichloromethyl-1,3,5-triazine (XXIII).—Of a saturated solution of ammonia in ether (at 0°), 16 ml. was diluted with 15 ml. of ice-cold absolute ether. To this solution 5 g. of XIX was added in small portions and the whole reaction contents kept at 0° for 2 hr. with occasional shaking. Upon filtration, 0.3 g. of a white solid was obtained which proved to be starting material. The ethereal filtrate was freed from ether on the steam-bath whereby a yellow oil remained which, to a large extent, crystallized upon cooling and repeated scratching of the wall of the flask with a glass rod. By vacuum-filtration 1.8 g. of white needles (XXIII, yield 54%) was obtained which were insoluble only in water but soluble in all common organic solvents. After several recrystallizations from a 50% dioxane–water mixture, XXIII was obtained as glittering leaflets, m.p. 130–131°.

Anal. Calcd. for $C_7H_7Cl_3N_4O_2$: C, 29.44; H, 2.47; Cl, 37.26. Found: C, 29.39; H, 2.56; Cl, 37.40.

2-Amino-4,6-bis-carbethoxy-1,3,5-triazine (XXIV).—A solution of ammonia in ether (19 ml.), saturated at 0°, was diluted with 15 ml. of ice-cold absolute ether. Into this solution 5 g. of XX was introduced and the reaction contents kept at 0° for 3 hr. with occasional shaking. During this time a voluminous precipitate (2.9 g.) had formed which upon investigation was found not to be homogeneous. By extraction with boiling ether, it could be separated into two components. The ether-soluble part proved to be unchanged starting material (XX), which was also obtained from the ethereal mother liquor of the original precipitate. The total amount of XX recovered was 4.0 g. (80%).

The ether-insoluble portion amounted to 0.4 g., melted at 179–180° and could be obtained by recrystallization from acetone–water (1:5) as white, small leaflets melting at 182–183°.

Anal. Calcd. for $C_9H_{12}N_4O_4$: C, 45.00; H, 5.04; N, 23.23. Found: C, 44.74, 44.94; H, 5.09, 5.33; N, 23.15, 23.14.

2-Amino-4-hydroxy-6-carbamyl-1,3,5-triazine (XXVII).—Five grams of XIX was added slowly with stirring to 40 ml. of concd. aqueous ammonia at room temperature and then kept for 6 hr. on the steam-bath. The somewhat cloudy hot solution was vacuum filtered and the filtrate allowed to cool down, whereby 0.3 g. (16.9% yield) of glittering crystals came off which had no melting point up to 400° and were identified as XXVIII.

Upon evaporation of the aqueous filtrate to dryness, 1.8 g. of a white substance was obtained. This substance, being insoluble in all common organic solvents and being soluble in hot water only, proved to be a hydrate of XXVII. Attempts to remove the hydrate water by heating the substance *in vacuo* resulted in partial decomposition of the material. Therefore for analysis the product was dried *in vacuo* for 1 hr. at 56°. It decomposed then in the melting point tube at 168–173°. The analysis of this sample indicated the presence of 2.5 moles of water.

Anal. Calcd. for $C_4H_5N_5O_2 \cdot 2.5H_2O$: C, 24.01; H, 5.04; N, 35.00. Found: C, 24.03; H, 5.51; N, 35.65.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

1,4-Addition of Grignard Reagents to 9-Phenanthryl Ketones[1]

BY REYNOLD C. FUSON AND STANLEY J. STRYCKER

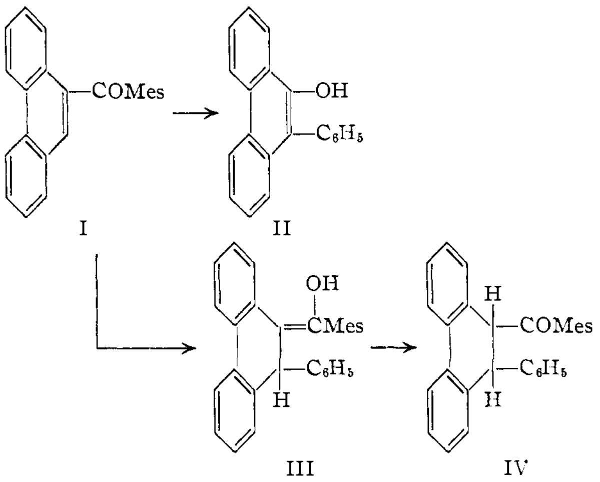
RECEIVED DECEMBER 20, 1956

It has been shown that 9-phenanthryl mesityl ketone reacts in the 1,4-manner with the methyl and phenyl Grignard reagents to give the corresponding 10-substituted 9,10-dihydrophenanthrenes. 9-Phenanthryl phenyl ketone and phenyl 9-phenanthrenecarboxylate react with phenylmagnesium bromide to yield phenyl 10-phenyl-9,10-dihydro-9-phenanthryl ketone.

The 1,4-addition of Grignard reagents to conjugated systems involving benzene rings, discovered 27 years ago by Gilman, Kirby and Kinney,[2] and almost at the same time by Kohler and Nygaard,[3] takes place more readily in the naphthalene series.[4] The difference, ascribed to the greater degree of double bond quality of the 1,2-bond in naphthalene, would be expected to be even more pronounced in suitably constituted phenanthrene derivatives; the 9,10-double bond of phenanthrene is known to have a higher order of reactivity than the bonds in naphthalene. To test this idea, we have prepared certain 9-phenanthryl ketones and subjected them to the action of Grignard reagents.

Our experiments have shown that mesityl 9-phenanthryl ketone (I) does react in the conjugate manner with the phenyl and methyl reagents. The first experiment with phenylmagnesium bromide gave an intractable oil. Chromatographic separation on an alumina-packed column yielded a small amount of the original ketone and a new compound which proved to be a phenol. It melted at 143–144° and formed an acetate (m.p. 153–155°) and benzoate (m.p. 179–180°). The melting points of the three compounds checked those given by Koelsch[5] for 9-phenyl-10-phenanthrol (II), its acetate and its benzoate. The formation of the phenanthrol is reminiscent of the production of 2-phenyl-1-naphthol in the naphthalene series[4] and similarly may be ascribed to the air oxidation of the enol III. In a subsequent experiment the expected dihydro ketones IV were isolated.

Methylmagnesium iodide behaved in a similar manner, the dihydro compound V likewise being obtained in two forms. Our belief that the methylated ketones are the expected diastereoisomers is strengthened by the observation that, when heated with a palladium-on-charcoal catalyst, the isomer having the lower melting point (109–110°) was changed to the higher-melting (154.5–155.5°) compound.



In search of a less highly hindered carbonyl compound we tried phenyl 9-phenanthroate (VI). With phenylmagnesium bromide it gave 9-benzoyl-10-phenyl-9,10-dihydrophenanthrene (VIII), presumably by way of 9-phenanthryl phenyl ketone (VII). This idea was supported by the results of experiments with the benzoyl compound VII. With the phenyl reagent it yielded the same dihydro ketone VIII obtained from the ester. We were satisfied with the structure VIII for this ketone, isolated in only one form, when we found that it could be dehydrogenated. The aromatized ketone, 9-benzoyl-10-phenylphenanthrene (IX), was obtained in small amount directly from the reaction mixture produced by the treatment of the phenyl ketone VII with phenylmagnesium bromide.

The aromatization could be effected in 76% yield by treatment of the dihydro ketone with bromine. This method was successful also in the aromatization of the methyl ketone V and the phenyl ketone IV. In the latter case, however, the dehydrogenation was accompanied by an unexpected cleavage. The cleavage product that was isolated proved to be 9-phenylphenanthrene. If mesitoic

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[2] H. Gilman, J. E. Kirby and C. R. Kinney, THIS JOURNAL, **51**, 2252 (1929).

[3] E. P. Kohler and E. M. Nygaard, *ibid.*, **52**, 4128 (1930).

[4] R. C. Fuson, B. C. McKusick and F. W. Spangler, *ibid.*, **67**, 597 (1945).

[5] C. F. Koelsch, *ibid.*, **56**, 480 (1934).