[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE A AND M COLLEGE OF TEXAS AND FROM THE TEXAS ENGINEERING EXPERIMENT STATION]

The Reaction of 2,4-Dinitrophenylhydrazine with some Dicarbonyl Compounds and α-Substituted Carbonyl Compounds[1]

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The reactions between eleven dicarbonyl compounds and eight α-substituted carbonyl compounds and 2,4-dinitrophenylhydrazine (DNPH) in 2*N* hydrochloric acid and ethanolic phosphoric acid have been studied. At room temperature and in 2*N* hydrochloric acid, glyoxal and pyruvaldehyde yielded bis-2,4-dinitrophenylhydrazones (DNP's) although paper chromatography indicated the latter compound formed a small amount of a mono-DNP. Butanedione and 2,3-octanedione gave a mixture of the mono- and bis-DNP's while benzil and 1-phenyl-1,2-propanedione produced only the mono-derivative, the DNPH attack occurring on the 2-carbonyl group. The 1,3-dicarbonyl compounds yielded 1-(2,4-dinitrophenyl)-3,5-disubstituted pyrazoles and 1,5- and 1,6-dialdehydes formed only bis-DNP's. A mono- and a bis-derivative could be prepared from 2,5-hexanedione. The other α-substituted carbonyl compounds, when treated with DNPH at elevated temperatures in ethanolic phosphoric acid, yielded the corresponding bis-DNP and 2,4-dinitroaniline, suggesting a Weygand-type of mechanism. Dichloroacetal gave only glyoxal-bis-DNP while chloral produced chloroglyoxal bis-DNP and ethyl glyoxylate-DNP. Benzotrichloride and benzal chloride produced the anomalous benzoyl chloride-DNP and benzaldehyde-DNP respectively, thus supporting the proposal that the S_N1 mechanism of halide hydrolysis applies to these reactions.

INTRODUCTION

The reaction between 2,4-dinitrophenylhydrazine (DNPH) and dicarbonyl compounds has not been studied as to the effect of structure on the formation of the mono-2,4-dinitrophenylhydrazones (DNP) in preference to the bis-DNP's although several mono-DNP's have been reported.[4] The same reaction with α-substituents other than carbonyl groups has received some attention recently. For example, the same bis-DNP has been obtained from 2-methoxy-[5] and 2-chlorocyclohexanones[6] and the chloro group in the mono-DNP of the latter compound could be replaced by a methoxy substituent by refluxing in methanol.[7] The failure of α-bromoacetophenone-DNP to undergo analogous reactions was explained in terms of the different labilities of primary and secondary halogens.[8] Further, the attempted preparation of the DNP of chloral yielded a product which gave a nitrogen analysis for chloroglyoxal-bis-DNP[9] although only one ultraviolet absorption maximum was reported[10] in contrast to the two maxima characteristic of 1,2-dicarbonyl-bis-DNP's.[11] An analogous reaction was previously proposed for chloral and hydroxylamine but no experimental evidence was presented to support the proposal.[12]

In the reaction of excess DNPH with an α-substituted carbonyl-DNP (excepting dicarbonyls), it might be assumed that the replacement of the substituent by a solvolysis mechanism is the first step in the reaction as suggested by the formation of 2-methoxycyclohexanone-DNP from the 2-chloro-compound.[7] However, reaction of DNPH with this product should yield some disproportionation product similar to that found in the Weygand mechanism for osazone formation.[13] Further, such solvolysis of chloral would lead to an acyl chloride, an acid, or an ester, none of which would be expected to form a bis-DNP.

During the course of other investigations[11,14] it was necessary to prepare several DNP's. No literature could be found describing several of the DNP's and, in view of the unusual reactions observed in some cases, it was felt that the results obtained would be of interest. This article describes the products obtained in the reactions between DNPH and α-substituted acetals and carbonyl compounds, and from these data a new mechanism is proposed for certain α-substituted compounds.

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(4) (a) H. Reich and L. Hefle, Jr., *J. Org. Chem.*, **21**, 708 (1956). (b) C. J. Timmons, *J. Chem. Soc.*, 508 (1957).

(5) H. Adkins and A. G. Rossow, *J. Am. Chem. Soc.*, **71**, 3836 (1949).

(6) R. B. Loftfield, *J. Am. Chem. Soc.*, **73**, 4707 (1951).

(7) F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **74**, 4331 (1952).

(8) F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953).

(9) K. Yamaguchi, S. Fukushima, T. Tabata, and M. Ito, *J. Pharm. Soc. Japan*, **74**, 1327 (1954).

(10) K. Yamaguchi, S. Fukushima, T. Tabata, and M. Ito, *J. Pharm. Soc., Japan*, **74**, 1335 (1954).

(11) L. A. Jones and C. K. Hancock, *J. Am. Chem. Soc.*, **82**, 105 (1960).

(12) A. Hantzsch and W. Wild, *Ann.*, **289**, 285 (1896).

(13) (a) F. Weygand, *Ber.*, **73B**, 1259 (1940). (b) For an excellent proof of mechanism see E. M. Bamdas, K. M. Ermoldev, V. J. Maimud, and M. M. Shamyakin, *Chem. and Ind.*, 1195 (1959).

(14) L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960).

TABLE I

No.	Compound	DNP	M.P.[a]	Nitrogen, % Calcd.	Nitrogen, % Found	Lit. M.P.	Minor Products
			DNP's Obtained from Procedure A				
1	Glyoxal	bis	313d. (Nb., Py.)	26.8	26.7	328[b]	None
2	Pyruvaldehyde	bis	298d. (Nb., HA.)	25.9	25.9	313[b]	mono-DNP
3	Butanedione	mono[c]	174 (Cf.-Mt.)	—	—	175[d]	bis-DNP
4	2,3-Octanedione	mono[e]	89 (Mt.-H_2O)	17.4	17.3	—	bis-DNP
5	1-Phenyl-1,2-propanedione	mono[f]	185 (Hp.)	17.1	17.1	—	None
6	Benzil	mono[g]	185 (Xy.)	—	—	185[h]	None
7	Succinaldehyde	bis	280 (MCS.)	—	—	280[i]	None
8	2,5-Hexanedione	bis	260d. (Xy., Py.)	23.6	23.2	259[b]	mono-DNP
9	Glutaraldehyde	bis	185 (Xy., Py.)	24.3	24.3	195[k]	None
10	β-Methyl glutaraldehyde	bis	198 (EA.)	23.6	23.6	203[k]	None
11	α-Hydroxyadipaldehyde	bis	219 (Dx.-H_2O)	22.9	22.1	—	None
			DNP's Obtained from Procedure B				
12	Butanedione	bis	316 (Nb., HA.)	25.1	25.2	315[b]	None
13	2,3-Octanedione	bis	221 (Nb., HA.)	22.3	22.4	213[b]	None
14	1-Phenyl-1,2-propanedione	bis	265 (Nb., HA.)	22.0	21.9	260[b]	None
15	Benzil	bis	311d. (Nm., HA.)	19.6	19.5	318[l]	None
16	Chloroacetal	reg.[m]	157 (Bz.)	—	—	157[n]	None
17	Chloro-2-propanone	reg.	126 (Hp.)	—	—	126[o]	None
18	Diethylaminoacetal	bis-1[p]	313d. (Nb., Py.)	—	—	—	DNA[q]
19	Diethylamino-2-propanone	reg.	85 (Bz.)	22.6	22.1	—	None
20	Phenoxyacetal	reg.	131 (Bz.-Hp.)	17.7	17.7	—	None
21	Dichloroacetal	bis-1	313d. (Nb., HA.)	—	—	—	None
22	Chloral	bis[r]	259d. (EA.)	24.8	25.0	264[s]	None
23	Benzoin	bis-6	311d. (Nm., Nb.)	19.6	19.8	318[l]	DNA
			DNP's Obtained from Procedure D				
16	Chloroacetal	bis-1 (97)[t]	313d. (Nb.)	—	—	—	DNA (74)[t]
17	Chloro-2-propanone	bis-2 (81)	298d. (Nb.)	—	—	—	DNA (67)
18	Diethylaminoacetal	bis-1 (94)	313d. (Nb.)	—	—	—	DNA (88)
19	Diethylamino-2-propanone	bis-2 (34)	298d. (Nb.)	—	—	—	DNA (10)
20	Phenoxyacetal	bis-1 (99)	313d. (Nb.)	—	—	—	C_6H_5OH (73)[u]
21	Dichloroacetal	bis-1 (25)	313b. (Nb.)	—	—	—	None
22	Chloral	bis[q]	259 (Ea.)	—	—	—	DNP of CHO—COOEt[t]

[a] All melting points are uncorrected. Data in parenthesis indicate recrystallizing solvents. Nb. = nitrobenzene, Py. = pyridine, HA. = glacial acetic acid, Cf. = chloroform, Mt. = methanol, Hp. = heptane, Xy. = *m*-xylene, MCS. = methylcellosolve, EA. = ethyl acetate, Dx. = *p*-dioxane, Nm. = nitromethane. [b] C. Neuberg and E. Strauss, *Arch. Biochem.*, **7**, 211 (1945). [c] $\nu_{C=O}$ = 1675 cm.$^{-1}$ [d] Ref. 4a. [e] $\nu_{C=O}$ = 1701 cm.$^{-1}$ [f] $\nu_{C=O}$ = 1653 cm.$^{-1}$ [g] $\nu_{C=O}$ = 1676 cm.$^{-1}$ [h] C. F. H. Allan, *J. Am. Chem. Soc.*, **52**, 2955 (1930). [i] L. C. Keagle and W. H. Hartung, *J. Am. Chem. Soc.*, **68**, 1608 (1946). [j] See Experimental for details of preparation. [k] C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5267 (1951). [l] D. Y. Curtin and V. R. Proops, *J. Org. Chem.*, **19**, 820 (1954). [m] reg. = regular derivative. [n] F. Weygand, G. Eberhardt, H. Linden, F. Shäfer, and I. Eigen, *Angew. Chem.*, **65**, 525 (1953). [o] G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953). [p] The number refers to compound 1. [q] DNA = dinitroaniline. [r] *Anal.* Calcd. for $C_{14}H_9N_5O_8Cl$: Cl, 7.8. Found: Cl, 7.5. [s] Ref. 9. [t] Data in parenthesis are average yields. [u] Isolated as the tribromo derivative by steam distilling from acid solution into bromine water.

EXPERIMENTAL

All materials used in this study were obtained from commercial sources and, where necessary, purified to obtain physical constants in agreement with literature values. All melting points are uncorrected.

Procedure A. One equivalent of the dicarbonyl compound was added to one equivalent of DNPH contained in a saturated DNPH 2*N* hydrochloric acid solution and the mixture shaken for 1–2 hr. at room temperature. The solid was filtered, washed with distilled water until the washings were neutral, and finally purified by column chromatography using 60–100 mesh silica-magnesia (Florisil, Floridin Co.) as the fixed phase and redistilled heptane as the eluent. Although the mono-DNP's were mobile in this system, no well-defined bands were apparent and the elution was accomplished by volume fractions, obscuring accurate data on yields. Infrared spectra were obtained as confirmation of structure.

Procedure B. The bis-DNP's of 1,2-dicarbonyl compounds were prepared in nearly quantitative yields by refluxing 1 equivalent with 2 equivalents of DNPH contained in ethanolic phosphoric acid (Johnson's Reagent).[15]

Procedure C. The α-substituted carbonyl compounds were refluxed for 8 hr. with 3 equivalents of DNPH (Johnson's Reagent).[15] Following filtration of the bis-DNP formed, the filtrate was neutralized with sodium carbonate and, if a solid appeared, filtered. The precipitate was recrystallized from heptane and a mixed melting point obtained with an authentic sample of 2,4-dinitroaniline while the bis-DNP was identified by mixed melting point determination with the derivatives prepared by Procedure B.

Procedure D. The α-substituted carbonyl compounds were treated with 1 equivalent of DNPH (Johnson's Reagent)[15] at room temperature and, following filtration, the solid derivatives were recrystallized from suitable solvents. The yields ranged from 96–99%.

The results of these procedures are shown in Table I.

(15) G. D. Johnson, *J. Am. Chem. Soc.*, **73**, 5888 (1951).

2,5-Hexanedione-mono-DNP. When the dicarbonyl compound was treated with DNPH in 2*N* hydrochloric acid, a mixture of the mono- and bis-DNP was obtained as evidenced by the large increase in melting point upon successive recrystallizations. Consequently, equivalent amounts of DNPH and 2,5-hexanedione were refluxed in a minimum amount of pyridine for 4 to 5 hr. and then stirred into 20 volumes of water and filtered. A typical preparation using 2.0 g. of DNPH and 1.3 g. of 2,5-hexanedione gave 0.7 g. of the mono-DNP after two recrystallizations from heptane, m.p. 116–117°.

Anal. Calcd. for $C_{12}H_{14}N_4O_5$: N, 19.0. Found: N, 18.8.

1-(2,4-Dinitrophenyl)-3,5-dimethylpyrazole was prepared in near quantitative yields from 2,4-pentanedione by Procedure A and gave yellow-green needles after recrystallization from methanol (m.p. 121.5°, lit.[16] m.p. 122°, 119–120°).

1-(2,4-Dinitrophenyl)-3-methyl-5-phenylpyrazole. One equivalent of DNPH in glacial acetic acid was refluxed for 24 hr. with 1-phenyl-1,3-butanedione and the solution evaporated to dryness on a steam bath. The solid, purified by Procedure A, gave yellow-green prisms in 70% yield (m.p. 133–134°, lit.[16b] m.p. 128–129°). The 3-phenyl-5-methyl-isomer was not found in the reaction mixture.

Anal. Calcd. for $C_{16}H_{12}N_4O_4$: N, 17.3. Found: N, 17.0.

1-(2,4-Dinitrophenyl)-3,5-diphenylpyrazole was prepared from 1,3-diphenyl-1,3-propanedione by the above procedure. Glacial acetic acid in heptane (20% v/v) failed to elute the product from a silica-magnesia column and, following extrusion of the column, the product was extracted from the fixed phase with methanol and the solution evaporated to dryness. Two recrystallizations from methanol gave yellow needles in 65% yield (m.p. 150.5–151.5°, lit.[17] m.p. 151–153°).

Benzoyl chloride-DNP. A mixture of redistilled benzotrichloride (10.0 g.) and 3.0 g. of DNPH was heated to 175° for 5 hr. and was accompanied by the steady evolution of hydrogen chloride. After cooling, the solution was taken up in 50 ml. of ether and filtered. Successive recrystallization of the solid from benzene and ethanol gave 2.6 g. (53.5%) of the DNP, m.p. 228.5–229°, $\lambda_{max}^{CHCl_3}$ 370 mμ, ε 2.70 × 10⁴, λ_{max}^{NaOH} 457 mμ, ε 2.48 × 10⁴.

Anal. Calcd. for $C_{13}H_9N_4O_4Cl$: N, 17.5; Cl, 11.1. Found: N, 17.4; Cl, 11.2.

Benzaldehyde-DNP was prepared by refluxing 20.0 g. of redistilled benzal chloride in 100 ml. of xylene with 5.0 g. of DNPH for 6 hr. Recrystallization of the precipitate from xylene and glacial acetic acid gave 4.8 g. (74%) of orange-red needles, m.p. 236–237°, which showed no melting point depression with an authentic sample and whose infrared and ultraviolet spectra were identical with those of the reference compound.

Ethyl glyoxylate-DNP. Chloral (3.0 g.) was refluxed 48 hr. with 100 ml. of Johnson's Reagent[15] diluted with 200 ml. of 95% ethanol. The solid, 3.4 g. of chloroglyoxal-bis-DNP, was filtered and the alcohol evaporated from the filtrate at room temperature. Filtration and recrystallization from cyclohexane of the resulting solid gave 2.6 g. of *ethyl glyoxylate-DNP*, m.p. 126–127°. The infrared spectrum showed a carbonyl absorption of 1702 cm.$^{-1}$ (m) and an ether linkage absorption at 1230 cm.$^{-1}$ (s). The ultraviolet and visible spectra in chloroform and alcoholic sodium hydroxide have been previously reported.[14]

Anal. Calcd. for $C_{10}H_{10}N_4O_6$: C, 42.6; H, 3.6; N, 19.9. Found: C, 42.6; H, 3.6; N, 19.9.

Pyruvaldehyde-mono-DNP was prepared by saturating 2 l. of distilled water with DNPH and adding 10 ml. of a 45% aqueous solution of pyruvaldehyde. The solution was allowed to stand for 2 weeks and then evaporated to a syrup. The residue was placed on a silica-magnesia column and eluted with chloroform, the eluent evaporated, and water added to precipitate the yellow-green solid. Filtration, followed by recrystallization from methanol-water gave 0.07 g. of yellow needles, m.p. 169–170°.

Anal. Calcd. for $C_9H_8N_4O_5$: C, 42.9; H, 3.2; N, 22.2. Found: C, 43.3; H, 3.6; N, 22.1.

The infrared spectrum contained a carbonyl stretching absorption at 1690 cm.$^{-1}$ and $\lambda_{max}^{CHCl_3}$ 345 mμ, ε 2.29 × 10⁴, λ_{max}^{NaOH} 490 mμ; ε 3.08 × 10⁴. Paper chromatography[18] of the derivative showed a single spot at an R_f previously observed for an unknown compound obtained from the pyruvaldehyde—Procedure A reaction product.

RESULTS AND DISCUSSION

Dicarbonyl compounds. Under the conditions described for Procedure A, glyoxal formed only the bis-DNP although, in the absence of acid, the mono-derivative has been prepared.[4a] Paper chromatography of the pyruvaldehyde reaction product showed the bis-derivative to be present in large amounts. In addition, however, the presence of a minute amount of a second compound (not DNPH) was observed at an R_f within the range of values obtained for other mono-DNP's of aliphatic 1,2-dicarbonyl compounds and subsequently shown to be the pyruvaldehyde-mono-DNP (see Experimental). Butanedione and 2,3-octanedione, when allowed to react with DNPH in 2*N* hydrochloric acid, yielded both the mono- and bis-DNP's in sufficient concentration to isolate and identify although only one of the two possible mono-DNP's of the latter carbonyl compound was isolated as indicated by the infrared spectrum. The mono-derivatives of 1-phenyl-1,2-propanedione and benzil were formed exclusively under these same conditions. bis-DNP's of the above carbonyl compounds were conveniently prepared by refluxing in Johnson's Reagent,[15] the aromatic compounds requiring six to eight hours of reflux as compared to two hours for the aliphatic carbonyl compounds.

The 1,3-dicarbonyl compounds yielded 1-(2,4-dinitrophenyl)-3,5-disubstituted pyrazoles when reacted with DNPH, and although the 3,5-dimethyl derivative could be produced by Procedure A, the aromatic analogues gave gummy products which produced crystalline pyrazoles on refluxing in glacial acid. Reaction of the 1,4- 1,5- and 1,6-dialdehydes with DNPH in 2*N* hydrochloric acid yielded only the bis-DNP's, while 2,5-hexanedione gave a mixture of mono- and bis-derivatives, the mono-DNP of which could be prepared in acceptable yield and purity using pyridine as the reaction solvent. Interestingly, attempts to recrystallize the bis-DNP's of 2,5-hexanedione and α-hydroxyadipaldehyde from acidic solvents resulted in tars and the aliphatic 1,2-dicarbonyl-mono-DNP's disproportionated to the bis-DNP's under the same conditions, similar to the results obtained with glyoxal-mono-DNP[4a].

Several interesting examples of polychromism were

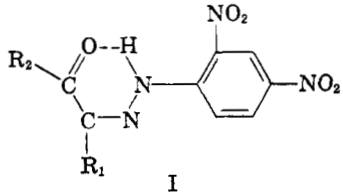
(16) (a) O. L. Brady, *J. Chem. Soc.*, 756 (1931). (b) W. Borsche and W. Reid, *Ann.*, **554**, 269 (1943).

(17) W. J. Croxall and J. O. Van Hook, *J. Am. Chem. Soc.*, **71**, 2422 (1949).

(18) R. B. Seligman, unpublished data.

found, the most striking being that of 1-phenyl-1,2-propanedione-bis-DNP, which gave orange-yellow needles when recrystallized from glacial acetic acid, red needles from nitrobenzene, and a mixture of the two from *m*-xylene. These had the same ultraviolet[11] and infrared spectra and identical melting points with no mixed melting point depression thus eliminating the possibility of *syn*- and *anti*-isomerism. The X-ray diffraction patterns indicated they were of different crystalline structures.[19]

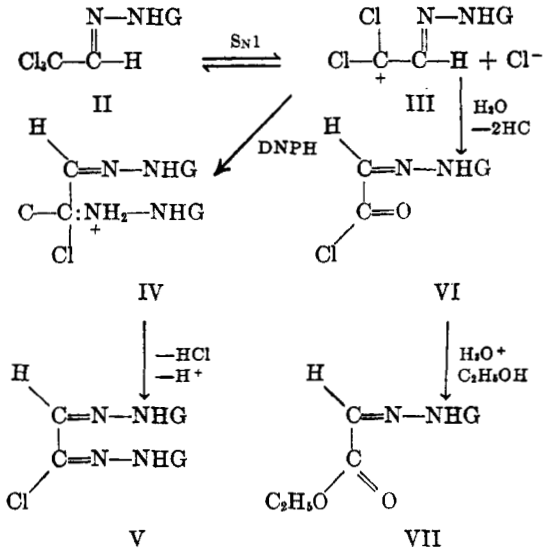
The infrared spectrum of 2,5-hexanedione-mono-DNP contains a carbonyl absorption at 1736 cm.$^{-1}$, characteristic of a nonconjugated carbonyl group. Suggestive of conjugative interaction between the C=O and the C=N moieties is the hypsochromic shift of 61 cm.$^{-1}$, observed in the carbonyl absorption of the corresponding derivative of butanedione. However, such interaction between C=C and C=N is reportedly small[20] and, by analogy, is probably small for the C=O and C=N linkages. Hence, the observed shift can be attributed to a combination of conjugation and hydrogen bonding of the type shown in I with no tautomeric shift of the *N*-hydrogen to the carbonyl oxygen occurring. These proposals are in accord with the ultraviolet spectra[11] and molecular models[21] of such derivatives.



I

In aromatic 1,2-dicarbonyl compounds the hydrazone formation occurs on the 2-carbonyl group as indicated by the carbonyl absorption occurring at 1653 cm.$^{-1}$ and the ultraviolet and visible spectra.[11] Further, 1-(2,4-dinitrophenyl)-3-methyl 5-phenyl-pyrazole could be formed only by the attack of DNPH on the 3-keto position of 1-phenyl-1,3-butanedione suggesting that the steric effect of the phenyl group is the determining factor in the position of the DNPH attack.

α-Substituted carbonyl compounds. The reaction of 1-chloro-2-propanone-DNP yielded pyruvaldehyde bis-DNP with excess DNPH, thus substantiating the proposal of Ramirez and Kirby that the action of DNPH on α-halo ketones involves the formation of an intermediate α-halo-DNP.[7] Isolation of 2,4-dinitroaniline and phenol following the reaction of excess DNPH with phenoxyacetal suggests the reaction proceeds by the same path as



G = 2,4-dinitrophenyl

Figure 1

osazone formation.[18] Benzoin reacted rapidly at room temperature to form the benzil-bis-DNP and α-hydroxyadipaldehyde-bis-DNP, on standing in a solution containing excess DNPH, slowly formed a solid which produced a blue color with alcoholic sodium hydroxide, characteristic of 1,2-dicarbonyl-bis-DNP's.[11] Attempts to increase the rate of reaction of α-hydroxyadipaldehyde-bis-DNP and DNPH by heating produced a tar and the reaction was not investigated further. From these reactions, however, it appears that α-hydroxy groups are particularly labile with respect to the disproportionation investigated.[18b]

Chloral and dichloroacetal, when allowed to react with DNPH, did not produce 2,4-dinitroaniline suggesting that the reaction does not proceed by the Weygand-type[18] mechanism. Further, the formation of chloroglyoxal-bis-DNP suggests that hydrolysis cannot be involved in the reaction since hydrolysis would yield an acyl halide which would not react to give the bis-DNP. With an excess of chloral, however, a mixture of chloroglyoxal-bis-DNP and ethyl glyoxylate-DNP was obtained and the reaction scheme shown in Fig. 1 appears reasonable in view of these results.

The equilibrium II ⇆ III is similar to that proposed for the S_N1 hydrolysis of benzyl halides[23] and the reaction VI → VII is in agreement with the proposed mechanism for the hydrolysis of benzotrichloride which produces benzoic acid.[24] The nucleophilic attack of DNPH on III must occur at a much faster rate than does the hydrolysis III →

(19) E. A. Meyers, unpublished data.

(20) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 268.

(21) Catalin Products, Ltd., Waltham Abbey, Essex, England.

(22) G. H. Stempel, Jr., and G. D. Schaffel, *J. Am. Chem. Soc.*, 66, 1158 (1944).

(23) E. D. Hughes, *Trans. Faraday Soc.*, 37, 603 (1941). See also S. C. J. Olivier and A. P. Weber, *Rec. Trav. Chim.*, 53, 869 (1934).

(24) J. Hine and D. E. Lee, *J. Am. Chem. Soc.*, 73, 22 (1951).

VI, as no ethyl glyoxylate-DNP could be found when the reaction was carried out at room temperature with excess DNPH. The product V cannot reasonably be obtained except through the unstable hydrazonium intermediate IV, and, with excess chloral, once the formation of V is complete, the remaining "mono-DNP" undergoes the hydrolysis-esterification reaction to VII.[25] The chloroform solution spectrum of V contained absorption maxima at 385 mμ (ϵ 4.01 × 10^4) and 435 mμ (ϵ 4.81 × 10^4) while in alcoholic sodium hydroxide λ_{max} 540 mμ (ϵ 5.42 × 10^4), the results being in complete agreement with the spectral properties previously reported for other bis-DNP's of 1,2-dicarbonyl compounds.[11]

The above reaction scheme implies that the trichloromethyl-group is activated by the conjugated unsaturation of the DNP moiety and, further, that a similar π-electron system should react in an analogous fashion. To test this hypothesis, DNPH was treated at elevated temperatures with an excess of benzotrichloride and yielded the anomalous "benzoyl chloride-DNP." Similarly, benzal chloride was used in the preparation of the benzaldehyde derivative. These results offer support for the reaction mechanism proposed and indicate that the DNP portion of the derivative has an activating effect similar to that of the phenyl groups in the benzyl halides.[28]

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(25) The mono-DNP of chloral, m.p. 131°, has been reported by F. L. Roduta and C. Quiblan, *Rev. Filipina med. farm.*, **27**, 123 (1936), *Chem. Abstr.*, **31**, 98. As the derivative was prepared from methanol, it seems likely the methyl glyoxylate DNP was the derivative isolated.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF LOWELL TECHNOLOGICAL INSTITUTE AND THE LOWELL TECHNOLOGICAL INSTITUTE RESEARCH FOUNDATION]

Chemistry of the Silylamines. I. The Condensation of Monofunctional Silylamines with Monofunctional Silanols[1]

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The rates of reaction of triphenyl- and triethylsilanol with a series of silylamines in bis(2-methoxyethyl) ether have been measured under a variety of conditions. The effect on the reaction rate of the structure of the reacting species, the addition of acid catalyst, and the observed second-order kinetics indicate a bimolecular type mechanism. This condensation reaction offers an alternate route for the formation of siloxane bonds.

Numerous reports in the literature indicate that silylamines are susceptible to attack by various nucleophilic reagents resulting in the cleavage of the silicon-nitrogen bond.

$$R{-}\underset{\displaystyle H}{\underset{|}{X}}{:} + \equiv Si{-}N{=} \longrightarrow R{-}X{-}Si{\equiv} + H{:}N{=}$$

X may be O, NH, or S

Rochow[2] states that an $-NH_2$ group attached to silicon is easily replaced by an —OH group upon hydrolysis, generating ammonia. The treatment of triethylsilylamine with hydrogen sulfide resulted in the formation of the corresponding thiol compound, triethylsilanthiol.[3] The reaction of hexamethyldisilazane with alcohols gives aliphatic trimethylsilyl ethers.[4] Langer and co-workers[5] have recently extended this reaction to prepare a large number of silyl ethers belonging to this class. Smith[6] has treated triethylsilanol with di-*tert*-butoxydiaminosilane and isolated $(C_2H_5)_3Si{-}O{-}Si{-}(t\text{-}C_4H_9O)_2{-}NH_2$.

In each of the above reactions of silylamines or silazanes with water, primary amines, alcohols, hydrogen sulfide, or a silanol, it appears that a nucleophilic displacement on silicon occurs,[5] which results in the formation of a new $\equiv$Si—O—, $\equiv$Si—N$=$ or $\equiv$Si—S— linkage.

Since this displacement reaction is of considerable practical importance for the synthesis of a variety of useful silicone intermediates and products, a program has been initiated in these laboratories to obtain fundamental information concerning the behavior of silylamines toward various nucleophilic reagents.

(1) Presented at the 137th meeting of the American Chemical Society, Division of Organic Chemistry, at Cleveland, Ohio, April 11, 1960.

(2) E. G. Rochow, *Chemistry of the Silicones*, John Wiley and Sons, New York, New York, 2nd ed., 1951, p. 58.

(3) E. Larsson and R. Mjorne, *Acta. Chem. Scand.*, **5**, 964 (1951).

(4) J. L. Speir, *J. Am. Chem. Soc.*, **74**, 1003 (1952).

(5) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(6) B. Smith, *Svensk. Kem. Tidskr.*, **65**, 101 (1953); *Chem. Abstr.*, **48**, 9907g (1954).