Anal. Calcd. for $C_6H_{12}Br_4Si$: C, 16.68; H, 2.80. Found: C, 16.86; H, 2.92.

A mixture of 21.6 g. (0.05 mole) of $(CH_3)_3SiCHBrCH_2CBr_3$ and 20.2 g. (0.2 mole) of triethylamine was heated at *ca.* 90° for 20 hr. After a short time white solid precipitated, and the solution became yellow, later brown. The mixture was filtered to remove 11.7 g. of triethylammonium bromide (m.p. 252–254° after recrystallization from methanol–ether). The filtrate was distilled to give 12 g. of light yellow liquid, b.p. 106–115° at 6 mm. Fractional distillation of the latter resulted in 9 g. (51%) of pure product, b.p. 94° at 3 mm., $n^{25}D$ 1.5458.

Anal. Calcd. for $C_6H_{11}Br_3Si$: C, 20.53; H, 3.16. Found: C, 21.11; H, 3.07.

The infrared spectrum was consistent with the assumed structure, $(CH_3)_3SiCH{=}CHCBr_3$, showing bands at 1592 cm.$^{-1}$ ($\nu_{C=C}$), 1250, 840 and 760 cm.$^{-1}$ (trimethylsilyl group). The absorption at 990 cm.$^{-1}$, indicative of a *trans*-1,2-disubstituted olefin, was very weak.

This compound did not react with I in toluene solution in the presence of benzoyl or *tert*-butyl peroxide at temperatures up to 145°.

Acknowledgment.—This work was supported by the United States Air Force under contracts no. AF 33(616)–7124 and AF 33(657)–8532, monitored by Materials Central, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. The authors are grateful to the Shin-Etsu Chemical Industry Co., Ltd., for granting a leave of absence to M. T. and to, the Silicone Products Department of the General Electric Company for gifts of silicon chemicals.

The Lithium Aluminum Hydride Reduction of Various Tetrahydropyridazine-1,2-dicarboxylic Acid Esters

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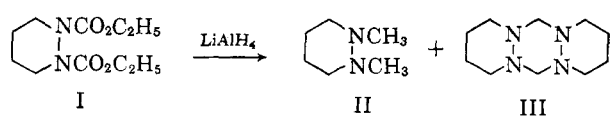
Several authors have described the Diels–Alder reaction between various dienes and azodicarboxylic acid esters and the subsequent reduction of the adducts to the tetrahydropyridazine-1,2-dicarboxylic esters.[1-8] This paper reports our investigation into the lithium aluminium hydride ($LiAlH_4$) reduction of certain of these esters.

The lithium aluminum hydride reduction of carbamates to the corresponding N-methyl compounds has been described,[9] but apparently this reaction has not been extended to hydrazino diesters. When diethyl tetrahydropyridazine-1,2-dicarboxylate[3,7] (I) was subjected to reduction by lithium aluminum hydride in ether, the major product formed was indeed 1,2-dimethylhexahydropyridazine (II). In addition, a small amount of a second product was obtained, which by analysis and infrared studies seemed to be 6*H*,13*H*-



I II III

octahydrodipyridazino[1,2-*a*:1′,2′-*d*]-*s*-tetrazine (III).

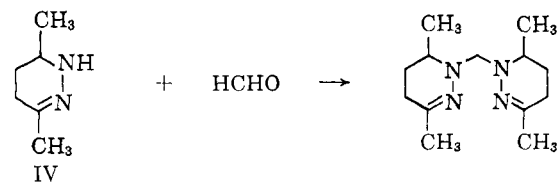
Confirmation of structure III was obtained by qualitatively identifying formaldehyde (as its 2,4-DNPH derivative) as one of the acid hydrolysis products of III and also by synthesis of III from hexahydropyridazine[3,7] and formaldehyde, as has been recently reported.[10] The product from the latter reaction was shown to be identical with that from the lithium aluminum hydride reaction by infrared comparison and mixed melting point.

Other esters of type I reduced by lithium aluminum hydride were the 4-methyl,[7] 4-isohexyl and 3,6-endomethylene[1] analogs. The products obtained along with several methiodide salts, are listed in Table I. The Diels–Alder adduct from chloroprene and diethyl azodicarboxylate was found to be unstable, liberating acidic vapors on standing. Catalytic reduction of the double bond in this adduct resulted in concurrent removal of the chlorine atom as well to give compound I.

The Diels–Alder addition between 1-methoxy-1,3-butadiene and diethyl azodicarboxylate gave the desired adduct, diethyl 3-methoxy-3,6-dihydro-1,2-pyridazinedicarboxylate, in high yield. Saturation of the double bond in this compound also proceeded satisfactorily. Attempted hydrolysis and decarboxylation of the diethyl 3-methoxy-3,4,5,6-tetrahydro-1,2-pyridazinedicarboxylate to the hexahydropyridazine caused complete disruption of the compound, due, undoubtedly to its hemiacetal type structure.

The reaction between diethyl azodicarboxylate and 1-diethylamino-1,3-butadiene[11] appeared to take place since the color of the diester was discharged, but no product could be isolated from the reaction mixture.

Substituted analogs of III were made by condensing various hexahydropyridazines with formaldehyde. (See Table II.) Using 3,6-dimethylhexahydropyridazine,[12] unsuccessful attempts were made to carry out this condensation with acetone, heptaldehyde, furfural, and thiophene carboxaldehyde in place of formaldehyde. The condensation of 2,3-diazabicyclo[2.2.1]heptane[1] with formaldehyde was likewise unsuccessful. It was found possible however, to effect the formaldehyde condensation with 3,6-dimethyl-1,4,5,6-tetrahydropyridazine[12] (IV).



IV

This reaction may thus have some utility in determining the positions of unsaturation in certain partially unsaturated nitrogen heterocycles.

It seems likely that the process by which III is formed from I must be similar to that by which III is

(1) O. Diels, *et al.*, *idib.*, **443**, 242 (1925).
(2) O. Diels and K. Alder, *Ann.*, **450**, 237 (1926).
(3) K. Alder and H. Niklas, *ibid.*, **585**, 81 (1954).
(4) O. Diels, *et al.*, *Ber.*, **71**, 1186 (1938).
(5) J. C. J. MacKenzie, *et al.*, *J. Org. Chem.*, **17**, 1666 (1952).
(6) S. G. Cohen, S. Hsiao, E. Saklod, and C. H. Wang, *J. Am. Chem. Soc.*, **79**, 4400 (1957).
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(8) W. T. Hunter, U. S. Patent 2,813,867 (November 19, 1957).
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(10) M. Rink and S. Mehta, *Naturwiss.*, **45**, 313 (1958).
(11) S. Hunig and H. Kahanek, *Ber.* **90**, 238 (1957).
(12) C. G. Overberger, N. R. Byrd, and R. B. Mesrabian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).

TABLE I

1,2-DIMETHYLHEXAHYDROPYRIDAZINES

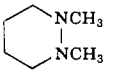
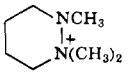
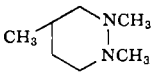
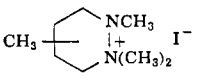
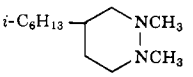
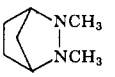
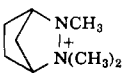
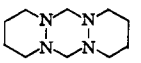
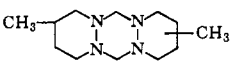
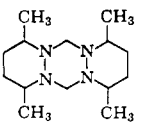
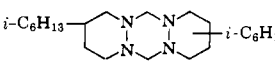
Compound	M.p. or b.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Iodine, % Calcd.	Iodine, % Found
	140–141 (atm.)	88	Analyzed as methiodide							
	248–249 dec.	62	32.82	33.03	6.69	6.51			49.55	49.88
	41–41.5 (20 mm.)	71	$n^{24.4}$D	1.45099	Analyzed as methiodide					
	232–232.5 dec.	98					10.37	10.30	46.98	46.79
	82-82.5 (1.5 mm.)	62	n^{26}D	1.45924			14.13	14.25		
	45–45.5 (24 mm.)	70	n^{25}D	1.46518	Analyzed as methiodide					
	227.5–228.5 dec.	80	35.83	35.83	6.39	6.15	10.45	10.52	47.33	47.14

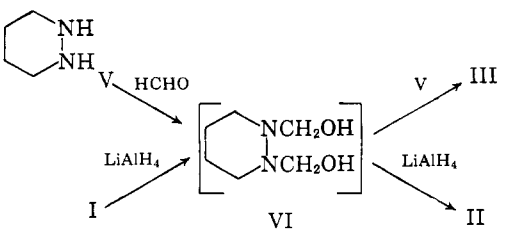
TABLE II

6*H*,13*H*-OCTAHYDRODIPYRIDAZO[1,2-*a*:1′2′-*d*]-*s*-TETRAZINES

Compound	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
	168–169[a]	89	61.18	61.07	10.27	9.97		
	188–189.5	52.5	64.24	64.31	10.78	10.49	24.98	25.81
	132.5–133	55	66.62	66.73	11.18	10.89	22.20	22.40
	174–175	12	72.47	72.58	12.16	12.68	15.37	15.27

[a] Literature[10] gives 168°.

formed from hexahydropyridazine (V) and formaldehyde, in that they both proceed *via* a common intermediate (VI).



This mechanism necessitates, however, that a small amount of either I or VI be converted to V by lithium aluminum hydride.

Experimental[13]

Diethyl 4-Chloro-3,6-dihydro-1,2-pyridazinedicarboxylate.—A mixture of 176 g. (2 moles) of chloroprene in 200 cc. of xylene and 261 g. (1.5 moles) of diethyl azodicarboxylate was allowed to stand for 1 week. The excess chloroprene and xylene were then distilled on the steam bath at the aspirator and the residue distilled under high vacuum through a short, glass-spiral column. After a forerun of 65 g. of unchanged azo ester, there was obtained 271 g. (69%) of the name product boiling at 132–133° (1.25 mm.). This compound was found to liberate acid vapors on standing.

Anal. Calcd. for $C_{10}H_{10}ClN_2O_4$: C, 45.62; H, 5.76; N, 10.67. Found: C, 45.40; H, 5.50; N, 10.66.

Diethyl 3-Methoxy-3,6-dihydro-1,2-pyridazinedicarboxylate.—A solution of 42.0 g. (0.5 mole) of 1-methoxy-1,3-butadiene in 60 cc. of anhydrous ether was cooled at 10° while a solution of 69.6 g. (0.4 mole) of diethyl azodicarboxylate in 40 cc. of anhydrous ether was added slowly. Upon completion of the addition, the temperature was allowed to rise to 30° and stirring was continued for 5 hr. The excess olefin and ether were removed on the aspirator and the residue (106 g.) distilled under vacuum. There was obtained 96.0 g. (93%) of the adduct boiling at 124–125° (1.25 mm.); n^{24}D 1.46803.

Anal. Calcd. for $C_{11}H_{18}N_2O_5$: C, 51.15; H, 7.02; N, 10.85. Found: C, 51.10; H, 6.81; N, 10.82.

Diethyl 3-Methoxy-3,4,5,6-tetrahydro-1,2-pyridazinedicarboxylate.—A solution of 51.6 g. (0.2 mole) of diethyl 3-methoxy-3,6-dihydro-1,2-pyridazinedicarboxylate in 100 cc. of 95% ethanol was hydrogenated at 40 p.s.i. using 0.5 g. of platinum oxide catalyst. After removal of the catalyst, the alcohol was distilled on the aspirator and the residue (50 g.) vacuum distilled. A yield of 47.0 g. (90.4%) of the reduced ester, boiling at 115–116° (1.25 mm.), was obtained; n^{24}D 1.46016.

(13) Melting points were taken on a Fisher–Johns apparatus and are uncorrected. Analyses were performed by Mr. Gordon Ginther and associates of these laboratories.

Anal. Calcd. for $C_{11}H_{20}N_2O_5$: C, 50.75; H, 7.75; N, 10.76. Found: C, 50.55; H, 7.38; N, 10.41.

Diethyl 4-Isohexyl-3,4,5,6-tetrahydro-1,2-pyridazinedicarboxylate.—The Diels–Alder adduct from myrcene and diethyl azodicarboxylate[2] was catalytically reduced to the saturated diester in alcohol solution with 5% palladium-on-charcoal catalyst (1 g./10 g. ester) in yields of 88–90%. The product boiled at 148–149°(0.8 mm.); $n^{26.3}D$ 1.45973.

Anal. Calcd. for $C_{16}H_{30}N_2O_4$: C, 61.1; H, 9.62. Found: C, 61.1; H, 9.32.

Lithium Aluminum Hydride Reduction of Tetrahydropyridazine Esters.—A solution of the tetrahydropyridazinedicarboxylic ester in ether was added slowly, without cooling, to a threefold molar excess of lithium aluminum hydride in ether. After stirring for 1.5–2 hr. and treating with a minimum amount of water, the solids were filtered and washed with ether. The ether solution was dried over magnesium sulfate, the ether carefully distilled through a column and the residue distilled. Because of their volatility, most of these compounds were converted to their methiodides for analysis. All of these compounds are listed in Table I.

6*H*,13*H*-Octahydrodipyridazino[1,2-*a*:1′,2′-*d*]-s-tetrazines.—Hexahydropyridazine,[7] 4-methylhexahydropyridazine[7] and 3,6-dimethylhexahydropyridazine[12] have been previously reported. 4-Isohexylhexahydropyridazine [b.p. 84–84.5°(0.125 mm.)] was prepared by hydrolysis of the corresponding 1,2-dicarboxylic ester with 25% methanolic potassium hydroxide. The condensation of these hexahydropyridazines with formaldehyde was effected by adding the free bases slowly with cooling to one molar equivalent of 37% formalin solution. After standing at room temperature for 3 hr., the mixture was chilled and the product filtered off. Evaporation and chilling of the mother liquor gave a second crop of product. The recrystallization solvent was hexane. Physical constants are given in Table II.

A small amount (about 2%) of compound III crystallized in the lithium aluminum hydride reduction of diethyl tetrahydropyridazine-1,2-dicarboxylate when the ether solution was concentrated just prior to distillation (see above).

Bis(3,6-dimethyl-1,4,5,6-tetrahydro-1-pyradazyl)methane.—To 72.3 g. (0.645 mole) of 3,6-dimethyltetrahydropyradazine[12] was added slowly and with cooling 26 cc. (0.32 mole) of 37% formalin solution. After standing overnight, the water was distilled under reduced pressure and the residue vacuum distilled. There was collected 70.6 g. (93.5%) of the name compound boiling at 99–102° (0.6 mm.). The distillate crystallized in the receiver. It was quite soluble in many organic solvents and was recrystallized from petroleum ether only at great loss. The product melted at 58–62°. This compound was unstable on standing.

Anal. Calcd. for $C_{13}H_{24}N_4$: C, 66.06; H, 10.23; N, 23.7. Found: C, 66.20; H, 9.72; N, 23.7.

Condensation of Hydroxynitroacetophenones with Aromatic Aldehydes in the Presence of Hydrogen Chloride

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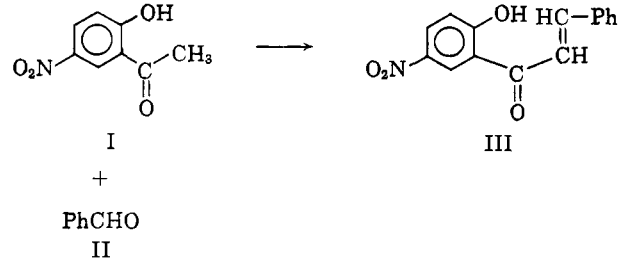
Received October 10, 1962

Acid catalysts ($AlCl_3$, BF_3, $ZnCl_2$, HF, HCl, H_2SO_4, AcOH, etc.) have long been used in the Claisen–Schmidt condensation of ketones and aldehydes.[1] Hydrogen chloride has been suggested by Wurtz,[2] Russel, and Lyle.[3] Schraufstätter and Deutsch state that this catalyst does not produce hydroxychalcones.[4] We have already shown that both basic and acidic catalysts can bring about the condensation of hydroxynitroacetophenones with aromatic aldehydes; the bases are the reagents of choice.[5,6]

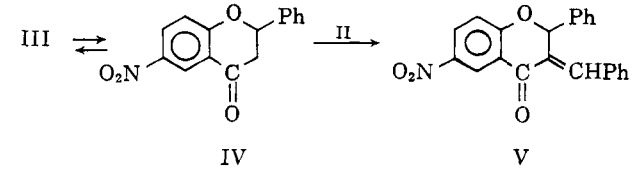
It has now been found that hydroxynitroacetophenones condense rapidly with aldehydes in alcoholic hydrogen chloride to form chalcones in satisfactory yield.



With an excess of aldehyde at higher temperature the condensation of 2-hydroxychalcones continues[7] and gives new products[5,8] which are formed also when the chalcone is employed as starting materials.

These compounds are regarded as 3-arylideneflavanones since they do not contain a hydroxyl group and are not identical with a number of other possible products. There is little likelihood of a Michael condensation between nitrochalcone and flavanone[9,10] and structural alternatives such as arylidenedi- and triacetophenones or dypnones can be excluded.[11]

The formation of V is believed to occur by cyclization of III in acidic medium and condensation of the flavanone (IV) with II. The cyclization is a known reaction



and flavanones contain an active methylene group which can undergo aldol-type condensations.[9,12] In the case of nitroflavanones the conversion to benzylidene derivatives has been realized experimentally in 80% yield. An alternative route involving the direct condensation of chalcones with aldehydes is considered unlikely since 3- or 4-hydroxynitroacetophenones, nitroacetophenones or benzoyloxynitrochalcone without free hydroxyl do not condense with II. Chalcones, unlike flavanones, do not contain an active methylene group which can undergo an aldol-type condensation.

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(2) A. Wurtz, *J. prakt. Chem.*, II, **5**, 457 (1872).

(3) A. Russel and J. Todd, *J. Chem. Soc.*, 1066 (1934); R. E. Lyle and L. P. Paradis, *J. Am. Chem. Soc.*, **77**, 6667 (1955).

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(7) With 5-nitro-2-hydroxyacetophenone this phenomenon has already been mentioned[5,8] but the structure of the compound formed was not satisfactorily determined.

(8) T. Széll, *Ann.*, **645**, 215 (1961).

(9) B. N. Kaplash, R. C. Shah, and T. S. Wheeler, *J. Indian Chem. Soc.*, **19**, 117 (1942).

(10) Durga Nath Dhar, *Agra Univ. J. Res.* **10**, 75 (1961).

(11) Gy. Sipos and T. Széll, *Naturwiss.*, **46**, 532 (1959).

(12) H. de Diesbach and H. Kramer, *Helv. Chim. Acta*, **179**, 1400 (1945); H. Kramer, thesis, University of Fribourg, 1944; Durga Nath Dhar, *J. Proc. Inst. Chem.*, **31**, 297 (1959).