acetic acid or Fenton's reagent did not furnish any crystalline materials.

1,3-Diphenyl-1,2-cyclohexanediol (VIII). The phenyl Grignard reagent was prepared from 25.2 g. (0.160 mole) of bromobenzene and 3.60 g. (0.150 g. atom) of magnesium in 50 ml. of ether. To this solution, a slurry of 7.34 g. (0.0386 mole) of 2-hydroxy-3-phenylcyclohexanone in 50 ml. of benzene was added. The deep gray-green mixture was heated under reflux for 2.5 hr. (solution temperature 56°). Hydrolysis was effected with an ice–ammonium chloride mixture. The *p*H of the aqueous layer was adjusted to 5–6 with dilute hydrochloric acid. After removal of the solvent from the organic layer, 5.47 g. (53%) of diol, m.p. 126–128°, was obtained. The analytical sample crystallized from a benzene-cyclohexane mixture in large cubic crystals, m.p. 129.5–131°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.53; H, 7.58.

Infrared spectral analysis of this diol on a high-resolution instrument demonstrated the existence of two types of O—H stretching absorptions: unassociated hydroxyl (3602 cm.$^{-1}$), and associated hydroxyl (3574 cm.$^{-1}$).[46]

5-Benzoyl-2-phenylpentanal (X). A mixture of 0.50 g. (1.9 mmoles) of 1,3-diphenyl-1,2-cyclohexanediol and 1.11 g. (2.5 mmoles) of lead tetraacetate in 15 ml. of benzene was heated under reflux for 1 hr. The mixture was filtered and the solvent removed; 0.41 g. (81%) of solid was obtained, m.p. 80–82°. Three crystallizations from a hexane-benzene mixture furnished the analytical sample, m.p. 84–85°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.09; H, 6.86.

The product, which decomposed upon exposure to air for a week, gave positive Tollens' and Benedict's tests. The infrared spectrum exhibited aldehyde absorption bands at 1718 and 2690 cm.$^{-1}$; the conjugated ketone absorption occurred at 1682 cm.$^{-1}$

5-Benzoyl-2-phenylpentanoic acid (XII). To a mixture of 0.42 g. (2.47 mmoles) of silver nitrate and 0.26 g. of potassium hydroxide in 5 ml. of water and 2 ml. of ethanol, 0.33 g. (1.24 mmoles) of 5-benzoyl-2-phenylpentanal was added. The reaction mixture was warmed for 0.5 hr. on a steam bath with stirring, then at room temperature for 2 hr. After filtration, the solution was acidified with dilute hydrochloric acid and then refrigerated. The crude acid (120 mg., m.p. 98–102°) was dissolved in base, the basic solution was extracted with benzene, and the acid was reprecipitated from the aqueous layer; 77 mg. (22% yield) of keto acid, m.p. 106–107°, was obtained. The analytical sample was crystallized from a hexane-benzene mixture and melted at 108–109°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.65; H, 6.55.

The neutralization equivalent was 286 (theoretical 282); acid bands (1702 cm.$^{-1}$, broad OH) and conjugated carbonyl absorption (1687 cm.$^{-1}$) were present in the infrared spectrum. Oxidation of the aldehyde with potassium permanganate gave the same product in about 8% yield. The neutral fractions from both oxidations were viscous yellow oils which appeared to be mixtures of carbonyl compounds, according to infrared analysis.

Chromic acid oxidation of 1,3-diphenyl-1,2-cyclohexanediol. A solution of 0.46 g. (1.71 mmoles) of the diol in 4 ml. of acetic acid was chilled in an ice bath; a solution of 0.37 g. (3.7 mmoles) of chromic anhydride in 2 ml. of water was added dropwise with stirring. The mixture was warmed slowly to 65°, at which temperature it was held for 2 hr. before addition to ice. Following benzene extraction, 0.40 g. of green crystalline material was obtained from which 0.18 g. (37%) of 5-benzoyl-2-phenylpentanoic acid, m.p. 107.5–108.5°, was isolated. This acid did not depress the melting point of a mixture with the product obtained in the previous experiment. The neutral fraction (0.16 g.) from the oxidation was purified by chromatography to yield 0.090 g. (21%) of fluffy platelets, m.p. 65–66°. This material was identified as 1,3-dibenzoylpropane by its infrared spectrum and by comparison with an authentic sample (m.p. 65–66°) prepared by the method of Japp and Michie.[47] That this diketone did not arise from oxidation of the keto acid was demonstrated by an attempted oxidation of the 0.11 g. of keto acid with 0.07 g. of chromic acid. No neutral component was isolated, and the acid fraction was a mixture, m.p. 71–103°, which could not be purified.

Camphoquinone was purified by crystallization from petroleum ether; m.p. 199–201°. The infrared spectrum contained two carbonyl bands: 1775 and 1759 cm.$^{-1}$ The 1759 cm.$^{-1}$ absorption was more intense than the 1775 cm.$^{-1}$ band. No hydroxyl absorption was present.

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(46) The authors are grateful to Mr. Page R. Edmondson of the Department of Medicine of the University of Minnesota for this determination on a calibrated Beckmann DK spectrophotometer. The spectrum of a 0.007*M* solution of the diol in carbon tetrachloride was measured in a 1-cm. quartz cell. An identical spectrum was obtained using a 0.0013*M* solution in a 5-cm. cell.

(47) F. R. Japp and A. C. Michie, *J. Chem. Soc.*, **79**, 1010 (1901).

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

α-Nitro Acid Chlorides. Preparation and Properties[1]

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March 3, 1959

α-Nitro acid chlorides can be prepared in good yields by chlorination of α-nitro acid hydrazides or their salts in inert solvents. They react rapidly with alcohols and ammonia to give α-nitro esters and amides and with sodium azide to give α-nitro acid azides.

Early attempts to prepare nitroacetyl chloride from nitroacetic acid by reaction with thionyl chloride or phosphorus pentachloride[2] failed and the acid chloride was synthesized only much later in small yield by the addition of nitryl chloride to ketene.[3] The higher homologs of nitroacetyl

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(1) (a) This work was performed under the auspices of the U. S. Atomic Energy Commission. (b) Presented before the Organic Section of the American Chemical Society at the 136th Meeting, Atlantic City, September 1959.

(2) W. Steinkopf, *Ber.*, **42**, 3925 (1909).

(3) W. Steinkopf and M. Kuhnel, *Ber.*, **75**, 1323 (1942).

chloride appear to be unknown except for certain perfluoro-α-nitro acid chlorides.[4]

During a study of α-nitro acid hydrazides and their salts,[5,6] the chlorination of these substances was investigated and it was found that they react with evolution of nitrogen and formation of acid chlorides as was reported for unsubstituted acid hydrazides.[7]

α-Nitro acid hydrazides belong to the activated acid hydrazides[8] which can be chlorinated directly without prior conversion to the hydrochlorides. α-Nitroisobutyrhydrazide, for instance, undergoes smooth chlorination at 0–20° to α-nitroisobutyryl chloride.

Since α-nitro acid hydrazides with α-hydrogens are usually obtained as hydrazine salts (I), these salts also have been chlorinated directly with excess chlorine. The products are the α-chloro-α-nitro acid chlorides (II), except in the case of nitroacethydrazide hydrazine salt which contains alcohol of crystallization and therefore yields esters. The same acid chlorides (II) are formed on chlorination of the hydrochlorides of the hydrazides (III), which result from the action of dry hydrogen chloride on the hydrazine salts I.[5]

$$\underset{\text{(I)}}{\mathrm{H_2N\overset{+}{N}H_3R\overset{-}{C}(NO_2)CONHNH_2}} \xrightarrow{\mathrm{Cl_2}} \underset{\text{(II)}}{\mathrm{RCCl(NO_2)COCl}}$$

$$\mathrm{I} \xrightarrow{\mathrm{HCl}} \underset{\text{(III)}}{\mathrm{RCH(NO_2)CONHN\overset{+}{H}_3\overset{-}{Cl}}} \xrightarrow{\mathrm{Cl_2}} \mathrm{II}$$

The α-nitro acid chlorides are colorless liquids which can be distilled from short-path stills. They react rapidly with water, alcohols, ammonia, and sodium azide. α-Nitroisobutyryl azide has been further identified by its conversion to the corresponding amide.

Chlorodinitroacetyl chloride (IV) represents a special case since it is the only α,α-dinitro acid chloride. It reacts readily with alcohols and sodium azide giving chlorodinitroacetates (V) and chlorodinitroacetazide. The reaction of chlorodinitroacetyl chloride with ammonia, however, results in complete destruction of the compound.

$$\underset{\text{(IV)}}{\mathrm{ClC(NO_2)_2COCl}} \qquad \underset{\text{(V)}}{\mathrm{ClC(NO_2)_2COOR}}$$

EXPERIMENTAL[9]

α-Nitro acid hydrazides. The preparation of the α-nitro acid hydrazides and their salts was described previously.[5] Dinitroacethydrazide hydrazine salt was prepared from ethyl dinitroacetate or the corresponding methyl ester.[6,10]

α-Nitro acid chlorides. The α-nitro acid hydrazide or its salt (0.01 mole), suspended in methylene chloride or alcohol-free chloroform (50 ml.), was treated with excess chlorine at 0°. The mixture was allowed to stand for 1 hr. at 0° (protected from moisture), warmed to 25° to complete the decomposition, and filtered from a little solid under dry nitrogen. Evaporation of the filtrate under 50 mm. pressure gave the crude acid chlorides in 79–96% yield. In view of their sensitivity to moisture, these products generally were used without further purification for the preparation of esters and amides, except as noted.

α-Nitroisobutyryl chloride was distilled from a molecular still.[11] It boiled at 30° (1.0 mm.) and had n_D^{25} 1.4391.

Anal. Calcd. for $C_4H_6ClNO_3$: N, 9.24. Found: N, 9.25.

On standing it hydrolyzed to the known α-nitro acid, m.p. 79–82° (lit. m.p. 95°[12]).

The infrared absorption spectra of the acid chlorides were determined in dichloromethane solution. Their characteristic absorption bands are given in Table I.

TABLE I

INFRARED ABSORPTION BANDS OF α-NITRO ACID CHLORIDES

	$\lambda_{C=O}$, μ,	λ_{NO_2}, μ, Asym	λ_{NO_2}, μ, Sym
$CCl(NO_2)_2COCl$	5.57	6.20	7.72
$CMeCl(NO_2)COCl$	5.57	6.30	7.52
$CMe_2(NO_2)COCl$	5.57	6.38	7.45

α-Nitro acid methyl esters. An exothermic reaction occurred when a solution of an α-nitro acid chloride (0.001–0.01 mole) in methylene chloride was mixed with an excess of methanol. The mixture was refluxed for 10–15 min. and evaporated under reduced pressure to remove the solvent. The liquid methyl esters were then distilled from a molecular still.[11]

The chlorination of the nitroacethydrazide hydrazine salt, m.p. 125° (dec.),[5] in methylene chloride directly furnished a solution of methyl esters which is regarded a evidence that the salt was a methanol solvate, as was proposed previously.[5] The reaction product, b.p. 55° (10 mm.), n_D^{25} 1.4356, was identified as a mixture of methyl chloronitroacetate and methyl nitroacetate[13] by gas chromatography[14] and infrared absorption spectra.

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[4] I. L. Knunyants and A. F. Fokin, *Doklady Acad. Nauk S.S.S.R.*, **112**, 67 (1957).

[5] H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, 22, 1662 (1957).

[6] L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, 23, 1340 (1958).

[7] L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 96 (1957).

[8] W. Davies, F. R. Storrie, and S. H. Tucker, *J. Chem. Soc.*, 624 (1931).

[9] All temperatures are corrected. Microanalyses by S. Yasuda and M. Naranjo.

[10] The formation of the hydrazine salt of ethyl dinitroacetate is accompanied by a small amount (2–6%) of carbon-carbon cleavage. With higher homologs of this ester, this is the main reaction, yielding the hydrazine salts of the 1,1-dinitroalkanes. The other cleavage product, ethyl hydrazinecarboxylate, has been isolated in all cases as the hydrochloride when the filtrates were treated with excess hydrogen chloride. It melted at 127–128° [lit. m.p. 129°, R. Stolle and A. Benrath, *J. pract. Chem.*, **70**, 276 (1904)] and was identical with an authentic specimen. *Anal.* Calcd. for $C_3H_9ClN_2O_2$: C, 25.64; H, 5.73; Cl, 25.22; N, 19.93. Found: C, 24.96; H, 5.98; Cl, 25.00; N, 19.51. The side reaction may be written:

$$\mathrm{HC(NO_2)_2COOEt + 2H_2NNH_2 \longrightarrow H\overset{-}{C}(NO_2)_2\overset{+}{N}H_3NH_2 + H_2NNHCOOEt}$$

[11] H. E. Ungnade, *Anal. Chem.*, **31**, 1126 (1959).

[12] W. Steinkopf and A. Supan, *Ber.*, **44**, 2895 (1911).

[13] The origin of methyl nitroacetate is explained tentatively by the intermediate formation of nitroacethydrazide hydrochloride under the influence of the liberated hydrogen chloride, its chlorination to nitroacetyl chloride, and the competitive methanolysis by methanol of solvation before the acid chloride can be further chlorinated.

[14] Gas chromatography by S. Yasuda.

(a) *Methyl α-chloro-α-nitropropionate,* b.p. 25° (0.2 mm.), had n_D^{25} 1.4313, yield 50%.

Anal. Calcd. for $C_4H_6ClNO_4$: C, 28.67; H, 3.61; N, 8.36. Found: C, 28.90; H, 3.59; N, 7.93.

(b) *Methyl α-nitroisobutyrate,* b.p. 30° (0.1 mm.), n_D^{25} 1.4195, yield 59%.

Anal. Calcd. for $C_5H_9NO_4$: C, 40.82; H, 6.16; N, 9.52. Found: C, 40.80; H, 6.41; N, 9.16.

(c) *Methyl chlorodinitroacetate,* b.p. 40° (4 mm.), n_D^{25} 1.4439, yield 66%.

TABLE II

INFRARED ABSORPTION BANDS OF α-NITRO ACID METHYL ESTERS[a]

	$\lambda_{C=O}$, μ	λ_{NO_2}, μ, Asym	λ_{NO_2}, μ, Sym	Other, μ
$CCl(NO_2)_2COOMe$	5.61	6.23	7.72	7.96
$CHCl(NO_2)COOMe$	5.66	6.32	7.45	7.67
$CMeCl(NO_2)COOMe$	5.67	6.36	7.46	7.89, 8.80, 9.08
$CMe_2(NO_2)COOMe$	5.69	6.42	7.40	7.79, 8.36, 8.56, 8.74

[a] Determined in capillary films.

Anal. Calcd. for $C_3H_3ClN_2O_6$: C, 18.15; H, 1.53; Cl, 17.86; N, 14.12. Found: C, 18.23; H, 1.51; Cl, 17.83; N, 13.78.

α-Nitro acid amides. The α-nitro acid chlorides (0.003–0.005 mole) were converted to amides by treating their solutions in methylene chloride or chloroform with anhydrous ammonia at 0°. The residues from the evaporation of the resulting solutions were crystallized from ether.

(a) *α-Chloro-α-nitropropionamide* was obtained in 54% yield as colorless needles, m.p. 81.5–82.5° (lit. m.p. 82°[15]), $\lambda_{C=O}$ 5.92μ, λ_{NO_2} 6.37, 7.47μ, λ_{NH} 2.99, 6.23μ.

Anal. Calcd. for $C_3H_5ClN_2O_3$: C, 23.62; H, 3.30; N, 18.37. Found: C, 23.84; H, 3.63; N, 17.90.

(b) *α-Nitroisobutyramide,* m.p. 120–121° (lit. m.p. 117–118°[16]), crystallized in 91% yield and had $\lambda_{C=O}$ 5.91μ, λ_{NO_2} 6.47, 7.40μ, and λ_{NH} 2.95, 6.18μ. Its melting point was unchanged by vacuum sublimation.

Anal. Calcd. for $C_4H_8N_2O_3$: C, 36.37; H, 6.10; N, 21.22. Found: C, 36.52; H, 6.05; N, 21.23.

α-Nitro acid azides. Chlorodinitroacetyl chloride (0.01 mole) was partially converted to the azide when it was refluxed with sodium azide (1.36 g., 0.02 mole) in alcohol-free chloroform (50 ml.) for 1 hr. The conversion was completed by displacing the solvent with carbon tetrachloride and refluxing for 4 hr. The infrared spectrum of the solution was unchanged on further heating and consisted of the following major bands (in μ): λ_{N_3} 4.62 (m), $\lambda_{C=O}$ 5.75 (m), λ_{NO_2} 6.21 (s), 7.75 (m), and 8.25 (s). Displacement of the solvent by toluene and heating to reflux temperature at 580 mm. caused complete decomposition of the azide without any evidence of isocyanate formation.

α-Nitroisobutyryl chloride (0.42 g., 0.00277 mole), after refluxing for 1 hr. with sodium azide (1.95 g., 0.03 mole) in alcohol-free chloroform (40 ml.), was completely converted to the known α-nitroisobutyrazide[5] (λ_{N_3} 4.64μ, $\lambda_{C=O}$ 5.81μ, λ_{NO_2} 6.44, 7.45μ). The azide was further identified by ammonolysis with dry ammonia, which furnished the known amide[16] in 70% yield.

Infrared absorption spectra were determined with a Model 21 Perkin-Elmer spectrophotometer.

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(15) W. Steinkopf and A. Supan, *Ber.*, **43**, 3242 (1910).

(16) O. Piloty and B. G. Schwerin, *Ber.*, **34**, 1865 (1901)

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT,
E. I. DU PONT DE NEMOURS & CO., INC.]

Synthesis of Hydrocarbon Derivatives by the Wittig Synthesis. I. Distyrylbenzenes

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p-Xylylene dichloride reacted quantitatively with triphenylphosphine to give *p*-xylylene bis(triphenylphosphonium chloride). This was converted to a bis-phosphonium "ylide" by lithium ethylate in ethanol, which was in turn converted to a series of disubstituted distyrylbenzenes by reaction with appropriately substituted benzaldehydes. Certain of the 1,4-distyrylbenzenes were reduced to 1,4-bis(phenethyl)benzenes.

Distyrylbenzene (III; R = X = H) has been synthesized by a variety of methods, none of which gives particularly good yields. Bisdesoxybenzoin has been reduced to the corresponding carbinol[1] which was in turn dehydrated to give a fair yield of distyrylbenzene. A second method has been the addition of benzylmagnesium chloride, to terephthalaldehyde[2] or 4-stilbenecarboxaldehyde[3] followed by dehydration of the resulting carbinols. This method is limited in scope because of the reactivity of the Grignard reagent toward functional groups. A third method which has been employed is the Perkin or Kuhn condensation of phenylacetic acid and 4-stilbenecarboxaldehyde[3] with lead oxide accompanied or followed by decarboxylation to the olefin. Finally, the Meerwein condensation of stilbene-4-diazonium chloride with cinnamic acid has given distyrylbenzene in 35% yield.[4]

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(1) J. Schmitt, P. Comoy, J. Boitard, and M. Suquet, *Compt. rend.*, **242**, 649 (1956).

(2) H. Kauffmann, *Ber.*, **50**, 515 (1917).

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