p-Dibenzhydrylbenzene (IV).—Finely powdered II (0.8 g.) was added to a solution of lithium aluminum hydride (1.0 g.) in N-methylmorpholine (50 ml.),[17] and the mixture refluxed for one hour. It was then poured into ice-cold dilute sulfuric acid and the reaction product extracted with ether. The crystalline residue of the extract was recrystallized from glacial acetic acid and formed needles of m.p. 171° (literature[18] 172°).

Anal. Calcd. for $C_{32}H_{26}$: C, 93.7; H, 6.3; mol. wt., 410. Found: C, 93.3; H, 6.3; mol. wt., 423.

Diphenyldiphensuccindene (V).—In the manner described, 0.8 g. of III was reduced with 1 g. of lithium aluminum hydride in 50 ml. of N-methylmorpholine and the reaction product isolated as above. It crystallized from methyl isobutyl ketone in prisms of m.p. 286° (literature[19] 285–286°). The same product is obtained when III is reduced with zinc dust and acetic acid.[19]

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[17] For the use of N-alkylmorpholines in reactions of this type, see F. A. Hochstein, THIS JOURNAL, **71**, 305 (1949).

[18] F. Ullmann and C. Schlaepfer, *Ber.*, **37**, 2001 (1904).

[19] K. Brand and W. Muehl, *J. prakt. Chem.*, [2] **110**, 1 (1925).

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The Reactions of Aliphatic Nitro Compounds: Condensations with Isocyanates[1]

BY ROBERT NEILSON BOYD AND RICHARD LESHIN[2]

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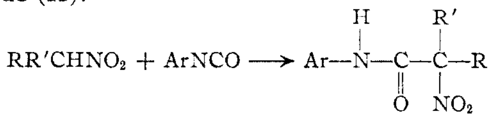
The reaction between the sodium salt of nitromethane and phenyl isocyanate has been found[3,4] to give ω(or α-)-nitroacetanilide (I) and nitromalonanilide (II).



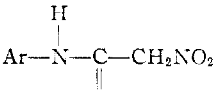
$$RR'CHNO_2 + ArNCO \longrightarrow Ar{-}\overset{\displaystyle H \atop |}{N}{-}\underset{\| \atop \displaystyle O}{C}{-}\overset{\displaystyle R' \atop |}{\underset{| \atop \displaystyle NO_2}{C}}{-}R$$

I, Ar = C_6H_5, R = H, R′ = H
II, Ar = C_6H_5, R = H, R′ = C_6H_5NHCO
III, Ar = C_6H_5, R = H, R′ = COOEt
IV, Ar = p-$NO_2C_6H_4$, R = H, R′ = COOEt

This reaction has now been extended to include the reaction of nitromethane and ethyl nitroacetate with 1-naphthyl, o-chlorophenyl and o-tolyl isocyanates to give a series of new N-substituted α-nitroacetamides and α-carbethoxy-α-nitroacetamides (Tables I and II).

TABLE I

N-ARYL α-NITROACETAMIDES



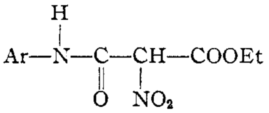
$$Ar{-}\overset{\displaystyle H \atop |}{N}{-}\underset{\| \atop \displaystyle O}{C}{-}CH_2NO_2$$

Aryl group	M.p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Phenyl	138[a]	$C_8H_8O_3N_2$	15.55	15.28
1-Naphthyl[b]	159–160[c]	$C_{12}H_{10}O_3N_2$	12.17	11.58
o-Chlorophenyl	121–122[d]	$C_8H_7O_3N_2Cl$	13.06	12.83
o-Tolyl	133[e]	$C_9H_{10}O_3N_2$	14.43	14.28

[a] Found by Michael and Steinkopf (ref. 3, 4). [b] Calcd.: C, 62.60; H, 4.38. Found: C, 62.33; H, 4.58. [c] Recrystallized from water or toluene; white plates which retain static electricity. [d] Recrystallized from water; yellow crystals. [e] Recrystallized from benzene; white needles.

TABLE II

N-ARYL α-CARBETHOXY-α-NITROACETAMIDES



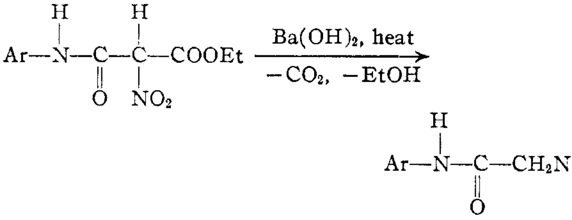
$$Ar{-}\overset{\displaystyle H \atop |}{N}{-}\underset{\| \atop \displaystyle O}{C}{-}\underset{| \atop \displaystyle NO_2}{CH}{-}COOEt$$

Aryl group	M.p., °C.	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
Phenyl[a]	100–101[b]	31	$C_{11}H_{12}O_5N_2$	11.11	11.37
1-Naphthyl[c]	124–125[d]	21	$C_{15}H_{14}O_5N_2$	9.27	9.42
o-Chlorophenyl	88[e]	55	$C_{11}H_{11}O_5N_2Cl$	9.77	10.11
o-Tolyl	86–88[f]	32	$C_{12}H_{14}O_5N_2$	10.52	10.63
p-Nitrophenyl	130–131.5[g]	12	$C_{11}H_{11}O_7N_3$	14.14	13.75

[a] Calcd.: C, 52.38; H, 4.80. Found: C, 52.68; H, 4.73. [b] Recrystallized from benzene–cyclohexane; white, curdy solid. [c] Calcd.: C, 59.60; H, 4.67. Found: C, 59.60; H, 4.45. [d] Recrystallized from benzene–cyclohexane; peach-colored needles. [e] Recrystallized from cyclohexane; white, curdy solid. [f] Recrystallized from benzene–cyclohexane; white, curdy solid. [g] Recrystallized from benzene; pale yellow needles.

It was not always found necessary to isolate the dangerously explosive sodium salt of nitromethane in order to effect a condensation; nitromethane could be condensed with phenyl and 1-naphthyl isocyanates in the presence of an equimolecular quantity of anhydrous potassium carbonate. The same base catalyzed all the condensations of ethyl nitroacetate.

Three compounds, III, V and VI were hydrolyzed and decarboxylated by hot barium hydroxide solution to give the corresponding N-substituted α-nitroacetamides (IIIa, Va, VIa).



$$Ar{-}\overset{\displaystyle H \atop |}{N}{-}\underset{\| \atop \displaystyle O}{C}{-}\overset{\displaystyle H \atop |}{\underset{| \atop \displaystyle NO_2}{C}}{-}COOEt \xrightarrow[-CO_2,\ -EtOH]{Ba(OH)_2,\ heat} Ar{-}\overset{\displaystyle H \atop |}{N}{-}\underset{\| \atop \displaystyle O}{C}{-}CH_2NO_2$$

III, Ar = C_6H_5 IIIa, Ar = C_6H_5
V, Ar = o-ClC_6H_4 Va, Ar = o-ClC_6H_4
VI, Ar = o-$CH_3C_6H_4$ VIa, Ar = o-$CH_3C_6H_4$

Nitroethane,[3,4] 1- and 2-nitropropane, phenylnitromethane, ethyl nitromalonate, nitromalonamide and bromonitromethane could not be condensed with phenyl isocyanate, either in the presence of potassium carbonate or when used in the form of their salts.

Experimental

N-Substituted α-Carbethoxy-α-nitroacetamides.—A typical preparation is that of N-phenyl-α-carbethoxy-α-nitroacetamide (III).

A mixture of 4.4 g. (0.033 mole) of ethyl nitroacetate, 40 ml. of dry benzene, 4.6 g. (0.033 mole) of anhydrous potassium carbonate and 4.0 g. (0.033 mole) of phenyl isocyanate was refluxed for three hours (or allowed to stand at room temperature for 2 weeks), during which time it was protected from moisture by a calcium chloride tube. The reaction mixture was cooled, and the precipitated material was collected, and then thoroughly stirred with 200 ml. of ice-water. The water-insoluble carbanilide (m.p. 238°) was removed and the aqueous filtrate was chilled and acidified to congo red, with constant stirring. The solution became opaque and after a short while a yellow-white precipitate appeared. The precipitate was collected after stirring an additional half hour, and was washed with cold water and dried in air. One recrystallization from benzene-cyclohexane gave 2.6 g. (31% yield) of a curdy, colorless solid (m.p. 100–101°).

N-Substituted α-Nitroacetamides.—N-Phenyl-α-nitroacetamide (I, α-nitroacetanilide) and N-(1-naphthyl)-α-

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[1] Presented at the 121st Meeting of the American Chemical Society at Buffalo, N. Y., March 25, 1952.

[2] Based on a portion of the dissertation submitted by Richard Leshin to the Department of Chemistry, New York University, February, 1952, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] A. Michael, *Ber.*, **38**, 22, 39 (1905).

[4] W. Steinkopf and H. M. Daege, *ibid.*, **44**, 497 (1911).

nitroacetamide were prepared in the manner described above for the derivatives of ethyl nitroacetate. It was necessary, however, to use the sodium salt of nitromethane in the preparation of the other two compounds in Table I. A typical preparation is that of N-(*o*-chlorophenyl)-α-nitroacetamide (V).

To a solution of 2.2 g. (0.036 mole) of nitromethane in 35 ml. of dry benzene, protected from moisture by a calcium chloride tube, was added 0.7 g. (0.030 mole) of sodium wire. After all the sodium had reacted, the benzene was decanted from the precipitated salt, which was then washed with several portions of dry benzene, and finally suspended in 35 ml. of dry benzene. To this suspension was added 5.0 g. (0.032 mole) of *o*-chlorophenyl isocyanate. The mixture was refluxed (the condenser was protected by a calcium chloride tube) for 2 hours, after which the solid reaction product was filtered off and washed with benzene. The solid was then added, portionwise, to 200 g. of crushed ice; an insoluble residue of 2,2′-dichlorocarbanilide (m.p. 238°)[5] was filtered off, and the aqueous solution was acidified to congo red. A yellow precipitate appeared, and after stirring for an additional half hour the product was filtered off, recrystallized once from water, and obtained as a yellow solid, m.p. 121–122°, in less than 10% yield.

Hydrolysis and Decarboxylation.—About 0.5 g. of the compound obtained by the reaction of ethyl nitroacetate with an isocyanate (except *p*-nitrophenyl isocyanate) was suspended in a large excess of a filtered saturated solution of barium hydroxide, and the mixture was boiled for about 5 minutes. After cooling, the mixture was acidified to congo red, and the solid residue was filtered off and recrystallized from water. In each case, the m.p. of the product was found to be the same as that of the corresponding compound prepared directly from nitromethane; furthermore, no depression of the m.p. was observed in any case for a mixture of a hydrolyzed and decarboxylated product with the corresponding direct condensation product.

Acknowledgments.—The nitroalkanes were a gift of Commercial Solvents Corporation. The analyses were done in the Microchemical Laboratory of New York University by Dr. W. C. Woodland and Professor T. S. Ma who supervised the laboratory, and their assistants, Dr. H. J. Stolten, Dr. R. H. Hansen, Mr. J. D. McKinley, Jr., and Mr. Paul Pemsler.

(5) C. Manuelli and E. Ricca-Rosellini, *Gazz. chim. ital.*, **29**, Part II, 128 (1899).

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Optical Dispersion of Perdeuterobenzene and Perdeuterocyclohexane

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In the course of some investigations being carried out in this Laboratory[1] on the physical properties of perdeuterobenzene and perdeuterocyclohexane the index of refraction of these compounds has been measured at three different wave lengths of light. It is the purpose of this note to record these index values and the various dispersion constants calculated from them.

The measurements were made with a Bausch and Lomb, Precision Abbe-type refractometer. The temperature of the prisms was maintained at 25.00 ± 0.02°. A sodium vapor light provided the light of wave length 5892.6 Å. (intensity-weighted mean of the doublet D_1,D_2). A mercury vapor lamp together with suitable filters provided the light of wave lengths 5460.7 and 4358.3 Å. The index of refraction of samples of N.B.S. Standard samples of 2,2,4-trimethylpentane and toluene, and of a purified sample of benzene, whose index had been previously checked against an NBS sample, was measured at each of the above wave lengths. Precautions were taken to ensure the purity of the samples, and in all cases the measurements were made on the samples immediately after their removal from sealed glass ampoules. From a comparison of the measured index values at each of the three wave lengths, with the certified values of their indices as reported by the National Bureau of Standards and tabulated by Forziati,[2] suitable instrument corrections were obtained. The instrument corrections were assumed to be a linear function of the refractive index reading, and did not appear to be a function of the wave length of the light used in the measurement. Correction values obtained on this basis were applied to the data reported here. The preparation of these deuterocarbons and their n_D values at 20° and 30° have been reported by Dixon and Schiessler.[3] Linear interpolations at 25° from their reported values are in excellent agreement with the values reported here. Table I lists the data for the deuterocarbons together with the data for the hydrocarbon isomers.

TABLE I

Wave length, Å.	Index of refraction at 25° C_6H_6[2]	C_6D_6[a]	C_6H_{12}	C_6D_{12}[b]
5892.6	1.49792	1.49597	1.42361	1.41909
5460.7	1.50197	1.49998	1.42544	1.42082
4358.3	1.51964	1.51798	1.43304	1.42802

[a] The purity of the C_6D_6 sample was equal to 99.3% replacement of protium with deuterium. Linear extrapolation of the measured value to 100.0% deuteration decreases the measured index by about 0.00001 which is less than the estimated uncertainty in the measurement. [b] The purity of the C_6D_{12} sample was equal to 98.8% deuteration. Linear extrapolation of the measured values to 100.0% purity decreases the measured index by about 0.00005 which is about the same as the estimated uncertainty in the measurement.

Forziati[2] has shown that the optical dispersion of organic compounds can be represented accurately by the modified Hartmann dispersion formula

$$n_\lambda = n_\infty + \frac{C}{(\lambda - \lambda^*)^{1.6}} \qquad (1)$$

where n_λ is the refractive index at light of wave length λ, and C, λ^*, and n_∞ are constants. The constants of this equation have been evaluated (after the construction of suitable tables for the wave lengths involved) by the method described by Forziati,[2] and are tabulated in Table II. Since the characteristic frequency ν_0 in the simplified Sellmeier–Drude[4–6] dispersion equation

$$n^2 - 1 = C/(\nu^2_0 - \nu^2_1) \qquad (2)$$

may be useful in the evaluation of the "London Dispersion Forces,"[7] the constants of this equation have been evaluated by the method of least squares and also are tabulated in Table II.

From equation 2 a value of the refractive index at infinite wave length may be calculated and this is also listed in Table II for comparison with the η_∞ calculated from the Hartmann equation.

Values of the Hartmann equation dispersion constants reported here for benzene are in good agree-

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(1) American Petroleum Institute Project 42. Advisory Committee: H. Sutherland, Chairman, E. M. Barber, J. R. Bates, L. C. Beard, Jr., G. H. Denison, L. M. Henderson, R. F. Marschner, L. A. Mikeska and J. H. Ramser.

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