tallized twice from benzene–petroleum ether, and once from petroleum ether alone, m.p. 117.5–119° (yield 75%).

Anal. Calcd. for $C_{12}H_9Br_3$: Br, 61.1. Found: Br, 60.1.

5-Bromoacenaphthene (IV, X = Br).—The cyclization of the dibromide (III, X = Br) was carried out as before, and the crude product dissolved in a mixture of methanol and ethanol. On scratching, a small amount of material, m.p. 90–102°, was obtained which was not investigated any further. The filtrate, upon concentration, left an oil which gave a very soluble picrate,[7] but afforded a very well-crystallized **trinitrobenzene complex**, m.p. 141–144° and after recrystallization from alcohol (elongated yellow rods) 144–146° (yield 55%).

Anal. Calcd. for $C_{18}H_{12}N_3O_6Br$: N, 9.4. Found: N, 9.3.

The TNB complex was decomposed by adsorption of its benzene solution on alumina and elution with ethanol. Evaporation and recrystallization from methanol gave 5-bromoacenaphthene in plates, m.p. 53–54° (literature[8] 52–53°).

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(7) The picrate, m.p. 114°, has been described by H. Crompton and M. Walker, *J. Chem. Soc.*, **101**, 958 (1912).

(8) M. Blumenthal, *Ber.*, **7**, 1092 (1874).

SCIENTIFIC DEPARTMENT
ISRAELI MINISTRY OF DEFENSE
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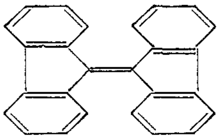
Highly Polarizable C=C Double Bonds (Fulvenes and Thermochromic Ethylenes. Part 28)[1]

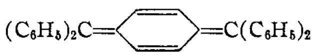
BY ERNST D. BERGMANN

RECEIVED JANUARY 7, 1953

Whilst the addition reactions of fulvenes with reagents typical for polar double bonds (metal-organic compounds,[2,3] lithium aluminum hydride,[4] donors in the Michael reaction,[5] can be explained by the polar character of the semicyclic double bond,[6,7] the analogous behavior of so symmetrical a substance as dibiphenylenethylene (I),[7,8] is very surprising. Bergmann, Fischer and Jaffe[9] and Lavie and Bergmann[1] have suggested that the "polar reactions" of I are due to the high *polarizability* of the central double bond. Indeed, the molecular refraction of I, which is a measure of the polarizability of the molecule, is unusually large, even in the infrared.[10,11] If this hypothesis is correct, other hydrocarbons which show the same phenomenon of an abnormally large molecular refraction, should be capable of reactions similar to I. This has been found to be true for tetraphenyl-*p*-quinodimethane (II) (*MR*, calcd., 138; *MR* found, 182 ± 4[12]), and diphenyldiphensuccindadiene (III) (for the corresponding dimethyl compound: *MR*, calcd., 75.5; *MR*, found, 86.5 ± 0.8[9,13]). *Both hydrocarbons add lithium aluminum hydride.* With this reagent, II gives in N-methylmorpholine as solvent a colored addition product, which, by hydrolysis, is converted into *p*-dibenzhydrylbenzene (IV). Analogously, III is transformed into diphenylsuccindene (V).

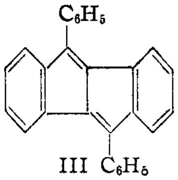


I

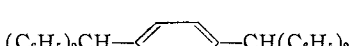


$(C_6H_5)_2C=C_6H_4=C(C_6H_5)_2$

II

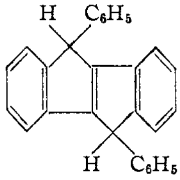


III



$(C_6H_5)_2CH-C_6H_4-CH(C_6H_5)_2$

IV



V

The spectrum of V (Fig. 1) shows a maximum (3225 Å., log ε 4.20) similar to that of the unsubstituted diphensuccindene (3100 Å., log ε 4.56[14]); a second maximum lies at 2400 Å. (log ε 4.25).

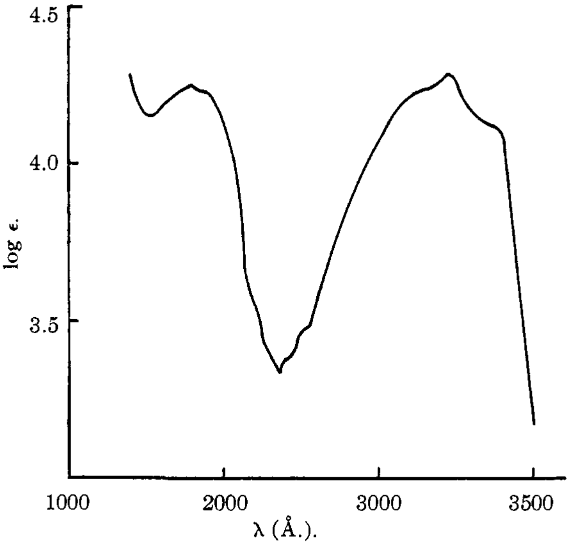


Fig. 1.—Diphenylsuccindene (V) in alcohol.

Experimental

Tetraphenyl-*p*-quinodimethane (**II**) was prepared according to Staudinger[15] (from xylene, m.p. 268°), **diphenyldiphensuccindadiene** (III) according to Brand[16] (from amyl alcohol, m.p. 260°).

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(1) Part 27, D. Lavie and E. Bergmann, *J. Org. Chem.*, **18**, in press (1953).

(2) K. Ziegler and W. Schaefer, *Ann.*, **511**, 101 (1934).

(3) R. C. Fuson and H. D. Porter, THIS JOURNAL, **70**, 895 (1948).

(4) D. Lavie and E. Bergmann, *Bull. soc. chim. France*, **18**, 250 (1951).

(5) L. A. Pinck and G. E. Hilbert, THIS JOURNAL, **68**, 2014, 2739 (1946).

(6) A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, **17**, 1097 (1950).

(7) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p. 333 ff.

(8) E. Bergmann, G. Berthier, A. Pullman and B. Pullman, *Bull. soc. chim. France*, **17**, 1079 (1950).

(9) E. Bergmann, E. Fischer and J. Jaffe, THIS JOURNAL, **75**, in press (1953).

(10) E. Bergmann and E. Fischer, *Bull. Israeli Research Council*, **1**, No. 4, 84 (1952).

(11) E. Bergmann and E. Fischer, *Bull. soc. chim. France*, **19**, 712 (1952).

(12) B. Pullman, A. Pullman, E. Bergmann, G. Berthier, E. Fischer, D. Ginsburg and Y. Hirshberg, *ibid.*, **18**, 707 (1951).

(13) B. Pullman, A. Pullman, E. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg and J. Pontis, *J. chim. phys.*, **49**, 24 (1952).

(14) L. F. Fieser and M. U. Pechet, THIS JOURNAL, **68**, 2577 (1946).

(15) H. Staudinger, *Ber.*, **41**, 1355 (1908); H. Staudinger and S. Bereza, *Ann.*, **380**, 276 (1911).

(16) K. Brand, *Ber.*, **45**, 3071 (1912).

***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).

LABORATORIES OF THE SCIENTIFIC DEPT.
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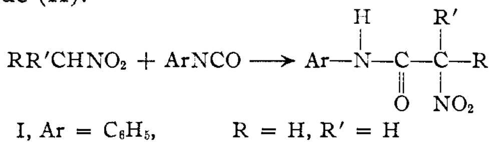
The Reactions of Aliphatic Nitro Compounds: Condensations with Isocyanates[1]

BY ROBERT NEILSON BOYD AND RICHARD LESHIN[2]

RECEIVED FEBRUARY 11, 1953

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).



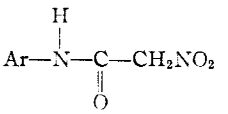
$$RR'CHNO_2 + ArNCO \longrightarrow Ar{-}\overset{H}{\overset{|}{N}}{-}\underset{\underset{O}{\|}}{C}{-}\overset{R'}{\overset{|}{\underset{\underset{NO_2}{|}}{C}}}{-}R$$

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



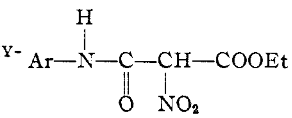
$$Ar{-}\overset{H}{\overset{|}{N}}{-}\underset{\underset{O}{\|}}{C}{-}CH_2NO_2$$

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



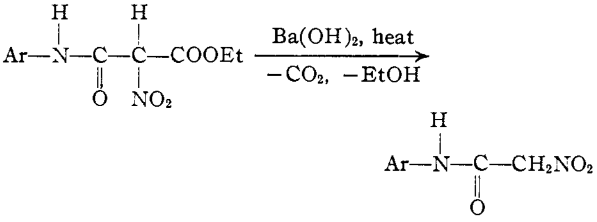
$$Ar{-}\overset{H}{\overset{|}{N}}{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{NO_2}{|}}{CH}{-}COOEt$$

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).



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

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).