TABLE I

Compound	M.p.,[a] °C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Fluorine, % Calcd.	Fluorine, % Found
4-TFA[b] biphenyl	200–201	95	5.28	5.42				
4,4'-Di-TFA biphenyl	324–325	98	7.45	7.13				
2-TFA fluorene	200–201	98					20.6	20.1
2,7-Di-TFA fluorene	300–301	92	7.2	7.4				
3-TFA dibenzofuran	204–205	97	5.02	5.10				
3-TFA dibenzothiophene	186–187	98			10.85	10.7		
2-TFA naphthalene	146–147	95	5.86	5.58				
2-TFA anthracene[c]	245–246	87						
4-TFA-2',3-dimethylazobenzene	158–159	90	13.1	12.8				

[a] All melting points are uncorrected. [b] TFA = Trifluoroacetylamino. [c] *Anal.* Calcd. for $C_{16}H_{10}F_3NO$: C, 66.44; H, 3.46. Found: C, 66.32; H, 3.82.

fluoroacetic anhydride.[15] In the case of 2,7-diaminofluorene 100 ml. of hot xylene was used as the solvent. After the initial reaction had subsided, the mixture was refluxed for half an hour. The cooled mass was filtered and washed with 10 ml. of cold benzene. Further product was obtained by evaporating the mother liquid under reduced pressure at room temperature. The fairly soluble acyl derivative of 2-naphthylamine was obtained by a similar evaporation of the reaction mixture. The diamine derivatives were crystallized from alcohol. The azo dye and the 4-aminobiphenyl derivative were crystallized from heptane. The 2-naphthylamine derivative was crystallized from aqueous alcohol while 2-trifluoroacetylaminofluorene was crystallized from benzene. These derivatives are more soluble than the analogous acetyl derivatives in non-polar solvents, such as heptane, and polar solvents, such as alcohol. The strong electronegative trifluoroacetyl group confers acidic properties on the new molecules for they are all soluble to some extent in aqueous sodium hydroxide solution.

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(15) Minnesota Mining and Manufacturing Co., St. Paul 6, Minnesota.

CANCER RESEARCH LABORATORY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

Formation of a Spiro Compound by the Action of Diazofluorene on Acenaphthylene

BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND NAZIH LATIF

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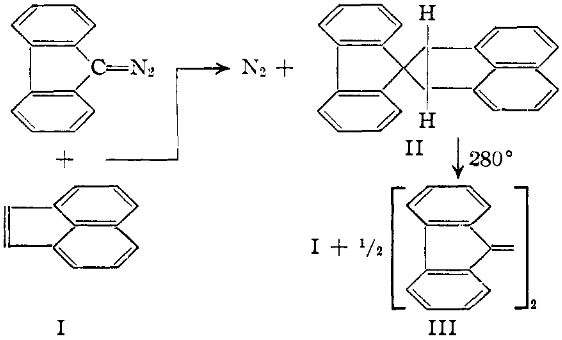
Though the action of diazomethanes on ethylenic compounds leading to three-membered rings has been observed frequently,[1] very little seems to be known about the formation of spiro products by this method. When acenaphthylene was treated with diazofluorene, the spiro product (II) was formed in good yield; in contrast with its generators and in agreement with the proposed formula, it is colorless. There seems to be some strain in (II) since it decomposes at 280° into acenaphthylene and $\Delta^{9,9'}$-bifluorene (III).



When acenaphthalene (I) was treated with an ethereal solution of diazomethane, it was recovered.

Experimental

Diazofluorene and Acenaphthylene.—A solution of 0.5 g. of acenaphthylene and 0.7 g. of 9-diazofluorene in 15 ml. of dry benzene was refluxed for 30 minutes. The mixture was allowed to stand overnight, concentrated and a few ml. of acetone was added to the residue. On standing, crystals separated which were recrystallized from benzene. 7,8–9',-9'-Fluorenyleneacenaphthene (II) is colorless, m.p. 275° (red-brown melt), yield about 80%.

Anal. Calcd. for $C_{25}H_{16}$: C, 94.9; H, 5.0; mol. wt., 316. Found: C, 94.4; H, 5.1; mol. wt. (micro-Rast), 282.

Thermal Decomposition.—A 0.5-g. sample of II was heated for one hour at 280–300° (bath temp.) in a test-tube shaped vessel (Pyrex glass) which was connected during pyrolysis to a working oil vacuum pump. The reaction vessel was then allowed to cool in a vacuum; the oily drops on the upper part of the tube solidified and proved to be acenaphthylene (m.p. and mixed m.p.). The bottom of the reaction vessel contained a red substance which was extracted several times with boiling ether. After concentration of the ethereal extract to about 1 ml., light petroleum (b.p. 40–60°) was added dropwise at room temperature to turbidity. A reddish-brown substance separated and was dissolved in a very small amount of hot benzene. The addition of a saturated benzene solution of picric acid yielded orange crystals overnight; these proved to be the picrate of $\Delta^{9,9'}$-bifluorene (III) (m.p. and mixed m.p.).

Diazomethane and Acenaphthylene.—An ethereal solution containing 1 g. of acenaphthylene and diazomethane[2] (prepared from 10 g. of nitrosomethylurea) was allowed to stand for 24 hours in the ice-chest. Acenaphthylene was recovered unchanged.

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(1) H. Wieland and O. Probst, *Ann.*, **530**, 277 (1937); P. C. Guha and S. Krishnamurthy, *Ber.*, **70**, 2113 (1937); W. Braren and E. Buchner, *ibid.*, **33**, 684, 3453 (1900).

(2) *Org. Syntheses*, **15**, 3 (1935).

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
FOUAD I UNIVERSITY
CAIRO, EGYPT

σ-Constants of the Carbethoxyl and Hydroxyl Groups

BY JOHN D. ROBERTS AND WALTER T. MORELAND, JR.[1]

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As part of another investigation,[2] we have had occasion to determine the σ-constants[3] of the *m*- and *p*-carbethoxyl and *m*-hydroxyl groups. The

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(1) U. S. Atomic Energy Commission Predoctoral Fellow, 1951–1952.

(2) J. D. Roberts and W. T. Moreland, Jr., THIS JOURNAL, **75**, 2167 (1953).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

TABLE I

σ-CONSTANTS FOR THE CARBETHOXYL AND HYDROXYL GROUPS

Reaction	Solvent	Temp., °C.	log $k^{\circ a}$	ρ^a	σ (m-$CO_2C_2H_5$)	σ (p-$CO_2C_2H_5$)	σ (m-OH)
Ionization of benzoic acids	H_2O	20	−4.234[b]	+1.107[b]	.....	.....	+0.040[b]
		25	−4.203[a]	+1.000[a]	.....	.....	+ .124[c]
	50% EtOH	25	−5.71[d]	+1.464[d]	+0.348	+0.437	+ .068
Benzoic acids with diphenyldiazomethane	100% EtOH	30	−0.014[d]	+0.937[d]	+ .313	+ .336	− .123
Alkaline hydrolysis of ethyl benzoates	87.83% EtOH	30	−3.072[a]	+2.498[a]	.....	+ .443[c]	.....
	56% acetone	25	−2.513[a]	+2.373[a]	+ .243[e,f,g]	+ .392[e,f]	.....
Phenols with acetyl bromide	Ethyl acetate	0	−1.170[h,i]	−1.898[h]	+ .341[i]	.....	.....
Methyl benzoates with aniline	Nitrobenzene	100	−0.898[j]	+0.379[h]	.....	.....	+ .040[j]
				Mean	+ .334	+ .402	+ .014

[a] Ref. 3. [b] Calculated from data of B. Jones and J. C. Speakman, *J. Chem. Soc.*, 19 (1944). [c] Calculated from the data of J. Shorter and F. J. Stubbs, *ibid.*, 1180 (1949). [d] Ref. 4. [e] Calculated after correcting the observed rate by a statistical factor of two. [f] Calculated from the data of E. Kivinen and E. Tommila, *Suomen Kemistilehti.*, **14B**, 7 (1941). [g] Not used in calculation of the mean. [h] Calculated from the data of H. L. Bassett, *J. Chem. Soc.*, 1313 (1930); 2516 (1931); H. L. Bassett and A. O'Leary, *ibid.*, 2945 (1932). [i] Relative value. [j] Calculated from the data of N. J. Vartak, N. L. Phalnikas and B. V. Bhide, *J. Indian Chem. Soc.*, **24**, 131A (1947).

reactions and procedures have been described previously in detail.[4,5]

The apparent ionization constants in 50% aqueous ethanol (by volume) at 25.0 ± 0.1° were 6.31×10^{-6}, 8.42×10^{-6} and 2.45×10^{-6} for *m*-carbethoxy, *p*-carbethoxy and *m*-hydroxybenzoic acids, respectively. The second-order rate constants with diphenyldiazomethane at 30.0 ± 0.1° in 100% ethanol were 2.16, 2.27 and 0.843, respectively, (all in l. mole^{-1} min.$^{-1}$) for the same series of substituted benzoic acids. The alkaline saponification rate of diethyl terephthalate in 87.83% ethanol at 30.0 ± 0.1° was 1.28 l. mole^{-1} min.$^{-1}$. The σ-constants from the available data are summarized in Table I.

The mean σ-values obtained from the data of Table I are: *m*-carbethoxyl, +0.334, r (the median deviation) equal to 0.014; *p*-carbethoxyl, +0.402, r equal to 0.038; and *m*-hydroxyl, +0.014, r equal to 0.076. A σ-value of −0.34 has been obtained previously[4] for the *p*-hydroxyl group.

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(4) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

(5) K. Kindler, *Ann.*, **450**, 1 (1926).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

The Solubility of Indium in Mercury

BY WILLIAM M. SPICER AND CYRIL J. BANICK

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In spite of the recent interest in alloys that are liquid at room temperature, the system mercury–indium has received little attention. Richards and Wilson[1] dissolved indium in mercury to the extent of 1.92% and found that the resulting amalgams are liquid at both 30 and 0°. Hildebrand[2] made amalgams containing up to 2.1% indium at 30°. Williams[3] in a study of the conductivity of liquid amalgams made an amalgam containing 3% indium. More dilute indium amalgams were used by Davies and Keeping.[4] None of these investigators attempted to determine the limit of the solubility of indium in mercury. Parks and Moran[5] investigated the solubility of indium in mercury over the temperature range 0–50°. They reported an increase in solubility from 1.23 weight % at 0° to 1.31 weight % at 50°.

It was in view of the paucity of the above data and their disagreement that this investigation was undertaken.

Preliminary tests indicated indium to be much more soluble than reported by Parks and Moran. It was therefore decided to investigate the entire range of compositions by means of cooling curves.

Experimental

The mercury used in this investigation was purified in the following manner. Air was bubbled through it for several hours to oxidize metallic impurities. It was filtered to remove the coarser particles of oxide and dirt, sprayed through a column of 3 N HNO_3, washed with distilled water to remove the acid and dried with filter paper. It was then vacuum distilled.

The indium used had a guaranteed purity of better than 99.97%. This high purity was confirmed by qualitative spectrographic analysis which showed only small amounts of cadmium and zinc. Its melting point was determined as 156.2°. There is considerable disagreement in the literature concerning the melting point of indium. Roth and Meyer[6] give 156.4°, Grube and Wolf[7] give 155°, while Denny, Hamilton and Lewis[8] give 156.1°.

An electric furnace for melting the alloys was constructed by modifying a tube furnace as follows. The furnace, which was approximately 15 inches in length with an opening approximately $^3/_4$ inch in diameter, was closed at one end with a plug of magnesia and arranged vertically. The outside wall of the furnace was wrapped with nichrome wire and covered with asbestos. This heating unit was left on while the sample was cooling to retard its rate of cooling. In this way rates of cooling ranging from 0.5 to 2.0° per minute were obtained.

This furnace was used in analyzing melts in the range beginning with those melting near pure indium down to about 60°. From this point, the furnace was replaced by a large tube with an air space to provide slower cooling. This outer tube was surrounded first by ice-water, then with

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(1) Theodore W. Richards and J. H. Wilson, *Z. physik. Chem.*, **72**, 129 (1910).

(2) Joel H. Hildebrand, THIS JOURNAL, **35**, 501 (1913).

(3) E. J. Williams, *Phil. Mag.*, **50**, 589 (1925).

(4) W. G. Davies and E. S. Keeping, *ibid.*, **7**, 145 (1929).

(5) W. G. Parks and W. G. Moran, *J. Phys. Chem.*, **41**, 343 (1937).

(6) W. M. Roth and I. Meyer, *Z. anorg. allgem. Chem.*, **214**, 315 (1933).

(7) G. Grube and W. Wolf, *Z. Elektrochem.*, **41**, 679 (1935).

(8) J. P. Denny, J. H. Hamilton and J. R. Lewis, *J. Metals*, **4**, 39 (1952).