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.

---

[15] Minnesota Mining and Manufacturing Co., St. Paul 6, Minnesota.

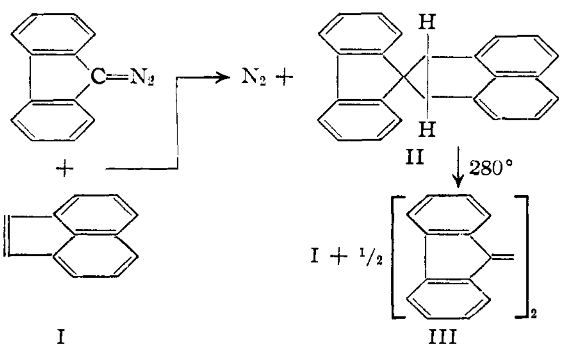
CANCER RESEARCH LABORATORY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA

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

BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND NAZIH LATIF

RECEIVED DECEMBER 22, 1952

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.

---

[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]

RECEIVED SEPTEMBER 2, 1952

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

---

[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.