in this case by the presence of an electron-withdrawing substituent on the phenyl ring.

EXPERIMENTAL[12]

Azibenzil. Azibenzil was prepared from benzil monohydrazone[13] by the method of Nenitzescu and Solomonica[10] with the following minor modifications: (*i*) the reaction mixture was cooled slightly before addition of the cold, alcoholic potassium hydroxide in order to minimize the frothing which accompanies the initial reaction; (*ii*) the crude azibenzil was dissolved in ether at room temperature and the solution was allowed to stand at room temperature for 1–2 hours, decanted from traces of mercury which otherwise always contaminated the product, and cooled at −20° overnight to effect crystallization. Pure azibenzil remained unchanged after storage at 0° in a dark, evacuated desiccator for several months.

Phenyldiazomethane. A solution of sodium hydroxide (8 g., 0.2 mole) in a mixture of water (15 ml.) and methanol (100 ml.) was added to a solution of azibenzil (5.56 g., 0.025 mole) in ether (125 ml.). The container was loosely stoppered and the mixture was allowed to stand at room temperature for 8 hr. Occasionally a small amount of white solid, possibly sodium benzoate, came out of solution early in the reaction, but homogeneity was restored by addition of small amounts of alcohol and/or water.[14] At the end of the reaction time a very small amount of pale yellow solid had been deposited (probably benzilazine[9]); this was removed by filtration and the clear, red solution was treated with 10% aqueous sodium hydroxide (100 ml.). The ethereal layer was washed with 10% aqueous sodium hydroxide (four 25-ml. portions) and dried over sodium sulfate, $\lambda_{max}^{CCl_4}$ 4.91 μ.

This ethereal solution of phenyldiazomethane was treated with *p*-nitrobenzoic acid in small amounts at a time until the solution was very pale yellow and further additions no longer caused gas evolution. The solution was washed with 5% aqueous sodium bicarbonate and with water, dried, and evaporated *in vacuo* to give benzyl *p*-nitrobenzoate (4.27 g., corresponding to a 71% yield of phenyldiazomethane); the infrared spectrum of the crude product showed only the bands of benzyl *p*-nitrobenzoate and one recrystallization from 95% ethanol gave the ester as shining plates, m.p. 82–82.5° (rec.[15] m.p. 83.5–84.5°) undepressed on admixture with an authentic sample. In another run, mandelic acid was used in a similar manner giving a yield of benzyl mandelate corresponding to a 70% yield of phenyldiazomethane; one recrystallization from ethanol gave material, m.p. 92.5–93.5° (rec.[16] m.p. 93°).

The aqueous basic layer and washings from the cleavage reaction were combined, cooled to 0°, acidified with dilute sulfuric acid, and extracted with chloroform. The chloroform extract was washed with water, dried, and evaporated *in vacuo* to give a dirty white solid (3.00 g.). An aliquot of the solid was sublimed for 8 hr. at a bath temperature of 60° and a pressure of 0.5 mm. to give a sublimate of benzoic acid and a residue of diphenylacetic acid, each identified by its infrared spectrum, m.p., and mixed m.p. The yields of benzoic and diphenylacetic acid were 90 and 6%, respectively.

4,4′-Dichlorobenzil monohydrazone. A solution of 95+ % hydrazine (3.5 g., 0.1 mole) in absolute ethanol (20 ml.) was added to a stirred, refluxing suspension of 4,4′-dichlorobenzil[17] (27.9 g.: 0.1 mole) in absolute ethanol (650 ml.). With the addition of the hydrazine, the ketone went into solution. The solution was refluxed for 30 min. and then distilled with continuous slow addition of water until approximately 350 ml. of distillate had been collected; the hydrazone began to separate after the removal of about 200 ml. of ethanol. The mixture was cooled in an ice bath and filtered: the hydrazone was washed with water and dried to constant weight *in vacuo* at 80°; yield, 28.1 g. (96%), m.p. 143–147° dec. Five crystallizations from absolute ethanol gave the hydrazone as fluffy, white crystals, m.p. 149.5–151.5° dec., $\lambda_{max}^{CH_2Cl_2}$ 2.92, 3.05, 6.08 μ.

Anal. Calcd. for $C_{14}H_{10}N_2OCl_2$: C, 57.36; H, 3.44; N, 9.56. Found: C, 57.60; H, 3.36; N, 9.68.

4,4′-Dichloroazibenzil. A suspension of 4,4′-dichlorobenzil monohydrazone (11.73 g., 0.04 mole), yellow mercuric oxide (30 g.: 0.14 mole) and anhydrous sodium sulfate (10 g.) in ether (150 ml.) was cooled to *ca.* 10° and treated with a few drops of cold, saturated ethanolic potassium hydroxide. A dark precipitate of mercury and mercury salts began to form immediately and the solution became dark orange-red. The suspension was shaken for 45 min. and then allowed to settle. The ethereal solution was decanted and the residual sludge was washed with ether by decantation until the washings were no longer colored. The combined solution and washings were allowed to stand for *ca.* 2 hr. to permit further separation of finely divided mercury, filtered, dried, and evaporated to a volume of about 100 ml. The solution was cooled at 0° overnight to give the diazoketone as shiny, orange spikes, m.p. 77–80° dec.; yield, 6.31 g. (54%); a small additional yield could be obtained by concentration of the mother liquors. Five recrystallizations from ether gave material, m.p. 91–92° dec., $\lambda_{max}^{CH_2Cl_2}$ 4.85, 6.14, 7.47 μ.

Anal. Calcd. for $C_{14}H_8N_2OCl$: C, 57.75; H, 2.77; N, 9.63. Found: C, 57.57; H, 2.82; N, 9.69.

Basic cleavage of 4,4′-dichloroazibenzil. The reaction of 4,4′-dichloroazibenzil with sodium hydroxide in ethereal-aqueous-methanolic solution was carried out exactly in the fashion used for the basic cleavage of azibenzil. Treatment of the orange-red, ethereal solution of the neutral product with benzoic acid and a few drops of boron trifluoride etherate gave a poor yield (*ca.* 50%) of a mixture of *p*-chlorobenzyl alcohol and *p*-chlorobenzyl benzoate (identified on the basis of the infrared spectrum). Acidification of the aqueous basic solution gave a 91% yield of *p*-chlorobenzoic acid, identified by infrared spectrum, m.p., and mixed m.p.

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[12] Melting points are uncorrected.

[13] L. I. Smith and H. H. Hoehn, *Org. Syntheses*, **Coll. Vol. III**, 357 (1955).

[14] Maintenance of homogeneity was found to be essential, since separation into two phases, leading to deposition of solid, drastically reduced the yield of phenyldiazomethane.

[15] R. Kothe, *Ann.*, **266**, 313 (1891).

[16] D. Base, *J. Am. Pharm. Assoc.*, **12**, 7 (1923).

[17] M. Gomberg and F. J. Van Natta, *J. Am. Chem. Soc.*, **51**, 2238 (1929).

Some Polyaryl Derivatives of Metals and Metalloids as Liquid Scintillator Solutes

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In previous surveys[1] of compounds screened as liquid scintillator solutes, an attempt has been made

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[1] (*a*) H. Kallman and M. Furst, *Nucleonics*, **8**, No. 3, 32 (1951); (*b*) F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, *Nucleonics*, **13**, No. 12, 38 (1955); (*c*) F. N. Hayes, D. G. Ott, and V. N. Kerr, *Nucleonics*, **14**, No. 1, 44 (1956); (*d*) V. N. Kerr, F. N. Hayes, and D. G. Ott, *J. App. Rad.*

to derive some generalizations regarding the effect exerted on their efficiency by various aromatic systems, position of attachment of polyaryls, heteroatoms, and various functional groups. In order to investigate any unusual effects caused by incorporating some less common heteroelements, a variety of polyaryl derivatives of various metals and metalloids (silicon, germanium, tin, lead, phosphorus, arsenic, antimony, and iron) were examined, and the results are listed in Table I. The compounds are generally inefficient scintillator solutes, and some are even mild quenchers.[1d]

TABLE I

PRIMARY-SOLUTE RELATIVE PULSE HEIGHTS

No.	Compound	Relative Pulse Heights	Ref.
1	Tetraphenylmethane	<0.10	*a*
2	Tetraphenylsilane	<0.10	*b*
3	Tris(*p*-dimethylaminophenyl)-(*p*-methoxyphenyl)silane	<0.10	*c*
4	Tetrakis(*p*-dimethylaminophenyl)-silane	<0.10	*c*
5	1,1,1,3,3,3-Hexaphenyldisilazane	<0.10	*d*
6	1-Naphthyltriphenylsilane	<0.10	*e*
7	2-Naphthyltriphenylsilane	0.14	*f*
8	Ethoxytri-1-naphthylsilane	<0.10	*e*
9	Tetra-3-biphenylylsilane	<0.10	*g*
10	Tetra-4-biphenylylsilane	0.29	*h*
11	*p*-Phenylenebis[triphenylsilane]	<0.10	*i*
12	Tetraphenylgermane	<0.10	*j*
13	Tetraphenyltin	<0.10	*k*
14	(*p*-Dimethylaminophenyl)triphenyltin	<0.10	*l*
15	1-Indenyltriphenyltin	<0.10	*m*
16	p-Phenylenebis[triphenyltin]	<0.10	*i*
17	Tetraphenyllead	<0.10	*n*
18	Tetrakis-(*p*-methoxyphenyl)lead	<0.10	*o*
19	Bis(*p*-dimethylaminophenyl)-diphenyllead	<0.10	*p*
20	Tetrakis(*p*-dimethylaminophenyl)-lead	<0.10	*p*
21	Triphenylphosphine	<0.10	*k*
22	Triphenylphosphine oxide	<0.10	*q*
23	Tris(2-biphenylyl)phosphine	<0.10	*r*
24	Tris(4-biphenylyl)phosphine	<0.10	*s*
25	Tris(2-biphenylyl)arsine	<0.10	*r*
26	Tris(4-biphenylyl)arsine	<0.10	*t*
27	Tris(2-biphenylyl)stibine	<0.10	*r*
28	Tris(4-biphenylyl)stibine	<0.10	*u*
29	Ferrocene	<0.10	*v*

[a] M. Gomberg and L. H. Cone, *Ber.*, **39**, 1463 (1906). [b] A. Polis, *Ber.*, **19**, 1013 (1886). [c] H. Gilman and M. A. Plunkett, *J. Am. Chem. Soc.*, **73**, 1686 (1951). [d] H. H. Reynolds, L. A. Bigelow, and C. A. Kraus, *J. Am. Chem. Soc.*, **51**, 3067 (1929). [e] H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, **73**, 4640 (1951). [f] H. Gilman, C. G. Brannen, and R. K. Ingham, *J. Am. Chem. Soc.*, **77**, 3917 (1955). [g] H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **21**, 1307 (1956). [h] W. C. Schumb, J. Ackerman, and C. M. Saffer, *J. Am. Chem. Soc.*, **60**, 2486 (1938). [i] H. Zimmer and H. G. Mosle, *Ber.*, **87**, 1255 (1954). [j] D. L. Tabern, W. R. Orndorff, and L. M. Dennis, *J. Am. Chem. Soc.*, **47**, 2039 (1925). [k] Commercially available. [l] H. Gilman and C. E. Arntzen, *J. Org. Chem.*, **15**, 994 (1950). [m] H. Gilman and L. A. Gist, *J. Org. Chem.*, **22**, 250 (1957). [n] H. Gilman and J. Robinson, *J. Am. Chem. Soc.*, **49**, 2315 (1927). [o] H. Gilman and J. C. Bailie, *J. Am. Chem. Soc.*, **61**, 731 (1939). [p] P. R. Austin, *J. Am. Chem. Soc.*, **54**, 3726 (1932). [q] A. Michaelis and H. v. Sodern, *Ann.*, **229**, 306 (1885). [r] D. E. Worrall, *J. Am. Chem. Soc.*, **62**, 2514 (1940). [s] D. E. Worrall, *J. Am. Chem. Soc.*, **52**, 2933 (1930). [t] D. E. Worrall, *J. Am. Chem. Soc.*, **52**, 664 (1930). [u] D. E. Worrall, *J. Am. Chem. Soc.*, **52**, 2046 (1930). [v] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

In all of the compounds screened the aromatic rings are separated from each other by the heteroatom, so that in no case are there more than two benzene rings joined directly (although Compounds 9 and 10 each contain eight benzene rings). The fact that Compound 10 has a marked relative pulse height while Compound 9 does not is further evidence of a previous observation, concerning the effect of position on these values, in the instance of the three terphenyls,[1a] *i.e.*, a *para* linkage<<*meta*<*ortho*. This effect was one of many which led to postulation of continuous resonance throughout the system[1b] as an important criterion in a scintillator solute. Obviously continuous resonance in *o*-terphenyls is prevented by lack of coplanarity, and in *m*-terphenyls by odd atoms, separating the terminal rings.

Included in the table are a variety of dimethylaminophenyl and methoxyphenyl derivatives (3, 4, 14, 18, 19, and 20), but even these groups, which have been shown to be beneficial to poor scintillator molecules in other instances,[1e,1f,1h,2] do not impart a measurable response to any of these compounds. Nor does the secondary amine function[1h] in hexaphenyldisilazane have any observable effect.

The failure to observe any values for the Group Vb elements is disappointing in view of the interesting results obtained with the corresponding nitrogen compounds. For example, although triphenylamine and diphenylamine gave very poor responses,[1a] tris(4-biphenylyl)amine (0.58) and bis-(4-biphenylyl)amine (0.95) proved to be quite efficient solutes.[1g] The failure of the biphenylylphosphine, -arsine, and -stibine compounds to scintillate, coupled with the quenching properties of the tetraphenyl derivatives of Group IVb metals, leads to the preliminary conclusion that elements beyond the first period of the periodic table are detrimental in scintillator molecules. This conclusion seems to hold for the halogens and for sulfur compounds in general.[1b] Perhaps incorporation of some of these elements in molecules which are otherwise good solutes would afford a more specific impression of the magnitude and reliability of this detriment.

The values reported in Table I were measured in the pulse height analyzer previously described,[1b] and all were measured at a concentration of 3 g./l.

Isotopes, **1**, 284 (1957); (*e*) H. Gilman, E. A. Weipert, T. Soddy, and F. N. Hayes, *J. Org. Chem.*, **22**, 1169 (1957); (*f*) H. Gilman, E. A. Weipert, J. J. Dietrich, and F. N. Hayes, *J. Org. Chem.*, **23**, 361 (1958); (*g*) H. Gilman, E. A. Weipert, R. O. Ranck, and F. N. Hayes, *J. Org. Chem.*, in press; (*h*) H. Gilman, E. A. Weipert, and F. N. Hayes, *J. Org. Chem.*, in press.

(2) J. R. Arnold, *Science*, **122**, 1139 (1955).

in toluene, except 19 and 20, which, due to limited solubility, were measured as saturated solutions. All values are relative to 2,5-diphenyloxazole which is assigned the arbitrary value of 1.00.

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The Constituents of *Casimiroa Edulis* Llave *et* Lex. IV.[1] Identification of Edulein with 7-Methoxy-1-methyl-2-phenyl-4-quinolone

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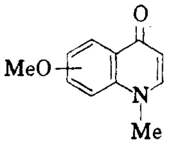
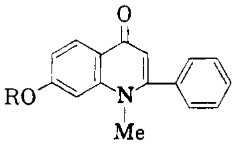
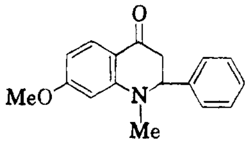
The isolation of the three new alkaloids edulein, edulitine, and edulinine from the bark of the tree *Casimiroa edulis* Llave *et* Lex, was reported in a previous paper of this series.[2] We now describe the elucidation of the structure of edulein through its identification with an alkaloid of known structure which was reported since our original paper was written.

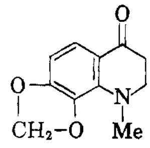
Edulein, $C_{17}H_{15}NO_2$, m.p. 201°, was previously shown to contain one methoxyl and one *N*-methyl group.[2] It was suggested that edulein contained an amide grouping since it was essentially neutral and the amide must have been tertiary in view of the absence of active hydrogen. Boiling edulein with potassium hydroxide in ethylene glycol has now given demethyledulein, $C_{16}H_{13}NO_2$, m.p. 324°, which no longer contains the methoxyl function. The substance is derived from edulein by cleavage of the methoxyl group to hydroxyl since methylation with diazomethane regenerated edulein. Boiling edulein with hydriodic acid likewise yielded demethyledulein and the alkaloid, like casimiroin,[1] is therefore very stable under both acidic and basic conditions.

The reduction of edulein with lithium aluminum hydride gave dihydroedulein, $C_{17}H_{17}NO_2$, m.p. 130°. The formation of this substance made the presence of an amide in edulein unlikely, since amides are generally reduced to the amines (involving loss of an oxygen atom) with lithium aluminum hydride.[3] The presence of a vinylogous tertiary amide of type I in edulein was indicated, since this would still account for the essentially non-basic character of the alkaloid and also for its reduction to a dihydro derivative. Such a formulation moreover lacks only a phenyl group to make up the complete structure of edulein.


I


IIa, R = Me
b, R = H


III


IV

At this stage of the investigation we were made aware through an interesting discussion with Dr. Sidney Goodwin (National Heart Institute, National Institutes of Health, Bethesda, Md.) of the similarity between edulein and an alkaloid isolated from the bark of *Lunasia amara* by Dr. J. R. Price *et al.* (Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia) and from the leaves by Dr. Goodwin *et al.* This alkaloid, which has been found to be 7-methoxy-1-methyl-2-phenyl-4-quinolone (IIa),[4] was shown by us by direct comparison to be completely identical with edulein. A difference seemed to lie in the picrates, since edulein picrate has been reported to have m.p. 192° [2] whereas the picrate of IIa has m.p. 220°.[5] The lower melting point of edulein picrate must have been due to polymorphism, since a new preparation showed the same melting point as the picrate of IIa and there was no depression on admixture. Edulein is therefore 7-methoxy-1-methyl-2-phenyl-4-quinoline (IIa) and demethyledulein is 7-hydroxy-1-methyl-2-phenyl-4-quinolone (IIb).

Dihydroedulein is comparatively non-polar, is not extracted from ether solution with mineral acids, and shows strong carbonyl absorption in the infrared (λ_{max} 6.01, 6.20, and 6.37 μ). It is most probably 7-methoxy-1-methyl-2-phenyl-4-keto-1,2,3,4-tetrahydroquinoline (III), derived from edu-

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(1) Part III, A. Meisels and F. Sondheimer, *J. Am. Chem. Soc.*, **79**, 6328 (1957).

(2) J. Iriarte, F. A. Kincl, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 4170 (1956).

(3) *Cf.* W. G. Brown, *Org. Reactions*, Vol. 6, Chapter 10, pp. 479–480 (1951); N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers Inc., New York, 1956, pp. 544–592.

(4) J. R. Price, *Fortschr. Chem. org. Naturstoffe*, **13**, 310 (1956).

(5) J. R. Price, private communication.