## EXPERIMENTAL

The compounds in Table II were synthesized by the method of Gabriel[9] from previously reported amides. The specific references for the amides are listed in the table.

Details concerning the experimental methods for obtaining the fluorescence spectra,[8] the ultraviolet absorption spectra,[8] and the pulse heights[6] may be found in previous papers. The infrared absorption spectra may be found in the Sadtler Standard Spectra.[10]

Los Alamos, N. M.

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[9] S. Gabriel, *Ber.*, **43**, 137 (1910).

[10] Samuel P. Sadtler and Son, Inc., Philadelphia, Pa.

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[Contribution from the Biomedical Research Group of the Los Alamos Scientific Laboratory of the University of California]

# Liquid Scintillators. VIII. The Effect of the Dialkylamino Group[1]

V. N. KERR, F. N. HAYES, D. G. OTT, R. LIER, AND E. HANSBURY

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A number of dialkylamino substituted 2,5-diaryloxazoles have been synthesized. The effect of the dialkylamino group upon the capability of these and other compounds to perform as liquid scintillator solutes is discussed.

Since 1955, this laboratory has maintained a screening program for potential liquid scintillator solutes.[2] A number of the solutes which contained the dialkylamino group were found to be rather good solutes when compared to the parent compound which would not scintillate at all. Since the time that the screening program was started, there have appeared in the literature a number of instances of the effect of this group upon liquid scintillator solutes.[3-10]

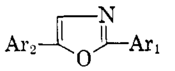
In addition to the beneficial effects of this group, it has also been noted that it can be harmful or ineffective.[5,8,9] The harmful effect of this group appeared with substitution in compounds which already had an appreciable pulse height. Evidently the beneficial effects are here outweighed by the quenching effect.[11]

Until now, observations on the effect of this group have been only incidental to other studies. The dialkylamino substituted oxazoles present an opportunity to study this group with a series of compounds which are notably good scintillator solutes.

It can be seen from Table I that the presence of

TABLE I

Pulse-Height and Spectral Data



| $Ar_1$ | $Ar_2$ | $I_{max}$[a] | $c_{max}$ | $\lambda_{max}^{fl}$ (mμ) | $\bar{\lambda}$ (mμ) | $\lambda_{max_1}^{abs}$ (mμ) | $\epsilon_1 \times 10^{-4}$ |
|---|---|---|---|---|---|---|---|
| $p$-$(CH_3)_2NC_6H_4$ | $C_6H_5$ | 0.95[b] | 3.2 | 403 | 428 | 345 | 4.08 |
| $C_6H_5$ | $p$-$(CH_3)_2NC_6H_4$ | 0.87 | 3.8 | 426 | 446 | 340 | 3.28 |
| $p$-$CH_3C_6H_4$ | $p$-$(CH_3)_2NC_6H_4$ | 0.85 | 4.2 | 420 | 440 | 339 | 3.38 |
| $p$-$CH_3OC_6H_4$ | $p$-$(CH_3)_2NC_6H_4$ | 0.97 | 6.4 | 414 | 426 | 337 | 3.80 |
| $p$-$(CH_3)_2NC_6H_4$ | $p$-$(CH_3)_2NC_6H_4$ | 0.69 | 2.5 | 422 | 450 | 355 | 4.52 |
| 1-$C_{10}H_7$ | $p$-$(CH_3)_2NC_6H_4$ | 0.66 | 3.3 | 470 | 492 | 360 | 2.62 |
| 3-Pyridyl | $p$-$(CH_3)_2NC_6H_4$ | 0.90 | 2.7 | 439 | 460 | 352 | 2.87 |
| *N,N*-Diethyl-4-biphenylamine[c] | | 0.62 | 6.1 | 368 | 373 | 301 | 3.00 |
| Biphenyl[c] | | ... | ... | 312 | 319 | ... | ... |

[a] Relative to 2,5-diphenyloxazole at 3 g./l. = 1.00. [b] Ref. (9). [c] Eastman Kodak, recrystallized.

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) Paper VII: Ref. 10.

[2] F. N. Hayes, V. N. Kerr, D. G. Ott, E. Hansbury, and B. S. Rogers, Los Alamos Scientific Laboratory Report *LA*-**2176**, Office of Technical Services, U. S. Dept. Commerce, Washington 25, D. C. (1958).

[3] J. R. Arnold, *Science*, **122**, 1139 (1955).

[4] H. Gilman, E. A. Weipert, T. Soddy, and F. N. Hayes, *J. Org. Chem.*, **22**, 1169 (1957).

[5] H. Gilman, E. A. Weipert, and F. N. Hayes, *J. Org. Chem.*, **23**, 760 (1958).

[6] H. Gilman, E. A. Weipert, and F. N. Hayes, *J. Org. Chem.*, **23**, 910 (1958).

[7] R. H. Wiley, C. H. Jarboe, Jr., and F. N. Hayes, *J. Org. Chem.*, **23**, 268 (1958).

[8] R. H. Wiley, *et al.*, *J. Org. Chem.*, **23**, 732 (1958).

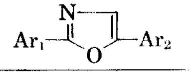
[9] D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, *J. Am. Chem. Soc.*, **79**, 5448 (1957).

[10] V. N. Kerr, F. N. Hayes, D. G. Ott, and E. Hansbury, *J. Org. Chem.* **24**, 1861 (1960).

[11] V. N. Kerr, F. N. Hayes, and D. G. Ott, *Intern. J. Appl. Radiation and Isotopes*, **1**, 284 (1957).

## TABLE II

### OXAZOLES



| $Ar_1$ | $Ar_2$ | M.P., °C.[a] | Formula | Carbon, %[b] Calcd. | Carbon, %[b] Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found | Yield, % | Corresponding Ketoamide Formula | Corresponding Ketoamide M.P., °C. | Corresponding Ketoamide Nitrogen, % Calcd. | Corresponding Ketoamide Nitrogen, % Found | Corresponding Ketoamide Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ | $p$-$(CH_3)_2NC_6H_4$ | 148–149.5 | $C_{17}H_{16}N_2O$ | 77.25 | 77.52 | 6.10 | 5.84 | 10.60 | 11.07 | 95 | $C_{17}H_{18}N_2O_2$ | 158.5–160 | 9.92 | 9.89 | 60 |
| $p$-$CH_3C_6H_4$ | $p$-$(CH_3)_2NC_6H_4$ | 174–176.5 | $C_{18}H_{18}N_2O$ | 77.67 | 77.60 | 6.52 | 6.27 | 10.07 | 9.92 | 91 | $C_{18}H_{20}N_2O_2$ | 188–191 | 9.45 | 9.58 | 51 |
| $p$-$CH_3OC_6H_4$ | $p$-$(CH_3)_2NC_6H_4$ | 134–135 | $C_{18}H_{18}N_2O_2$ | 73.45 | 73.55 | 6.16 | 6.28 | 9.52 | 9.54 | 94 | $C_{18}H_{20}N_2O_3$ | 187–188.5 | 8.97 | 8.94 | 58 |
| $p$-$(CH_3)_2NC_6H_4$ | $p$-$(CH_3)_2NC_6H_4$ | 206–208 | $C_{19}H_{21}N_3O$ | 74.24 | 74.32 | 6.89 | 6.95 | 13.67 | 13.83 | 87 | $C_{19}H_{23}N_3O_2$ | 244.5–251.5 | 12.91 | 12.83 | 31 |
| 1-$C_{10}H_7$ | $p$-$(CH_3)_2NC_6H_4$ | 117–118.5 | $C_{21}H_{18}N_2O$ | 80.23 | 80.16 | 5.77 | 5.92 | 8.91 | 9.03 | 64 | $C_{21}H_{20}N_2O_2$ | 150–152 | 8.43 | 8.30 | 47 |
| 3-Pyridyl | $p$-$(CH_3)_2NC_6H_4$ | 137–138 | $C_{16}H_{15}N_3O$ | 72.43 | 72.56 | 5.70 | 5.79 | 15.84 | 15.86 | 90 | $C_{16}H_{17}N_3O_2$ | 178.5–182 | 14.83 | 14.73 | 43 |

[a] All melting points were taken on a Fisher-Johns melting point block and are uncorrected. [b] Microanalyses by Micro-Tech Laboratories, Skokie, Ill. Solvents for recrystallization were either hexane or a mixture of hexane and toluene.

other substituents can considerably modify the effect of the dialkylamino group. When it is introduced into 2,5-diphenyloxazole, with no other substituents present, there is a resultant pulse height ($I_{max}$) drop, the extent of which is dependent upon the position of the substituent. When the *p*-dialkylamino group is on the 2-phenyl substituent of the oxazole, the drop is less than when this group is on the 5-phenyl substituent. The presence of the *p*-methoxyphenyl or the 3-pyridyl group prevents any large drop in pulse height. These alkylamino substituted compounds have a pulse height which is only slightly lower than that of the parent oxazole. A *p*-tolyl substituent is effectively the same as a phenyl group. The largest pulse height drop occurs when substitution is made in a compound which contains another alkylamino group or when one aryl substituent is the 1-naphthyl group.

Self-quenching is higher with the alkylamino substituted oxazoles as evidenced by the lower values for $c_{max}$. This could be anticipated since these compounds are more polar than the non-dialkylamino substituted oxazoles, and hence the chance for collisional deactivation is increased (since these molecules could be expected to have a more prolonged contact time).[12]

An instance of the striking beneficial effect of this group, as opposed to the effect on the oxazoles, can be seen with the diethylamino substituted biphenyl.[13]

Both the fluorescence and the ultraviolet absorption spectra show a bathochromic shift relative to the nonaminated compounds. The largest shift is shown in the fluorescence spectra with a maximum shift of up to 70 mμ. This bathochromic shift contributes largely to the increased pulse height of the substituted biphenyl, since the region of fluorescence of biphenyl is considerably below the sensitive region of the pulse height detector system.[14] The fluorescence spectra of the aminated oxazoles are structureless showing none of the shoulders or minor peaks which are associated with the other oxazoles. The bathochromic shift does not affect $I_{max}$ of the oxazoles, since the fluoresence spectra of both the aminated and the nonaminated oxazoles lie within the plateau region of the detector's spectral sensitivity curve.

In addition to the bands normally found in the ultraviolet absorption spectra of the oxazoles, there is a band at 270 ± 5 mμ, which is associated with the dialkylamino substituent. The extinction coefficient of the first absorption band is greater with the aminated oxazoles than with the nonaminated oxazoles.

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(12) E. J. Bowen and F. Wokes, *Fluorescence of Solutions*, Longmans, Green and Co., London, 1953, p. 31–33.

(13) This effect could be expected to have been greater had the alkyl groups been methyl rather than ethyl.[4,9]

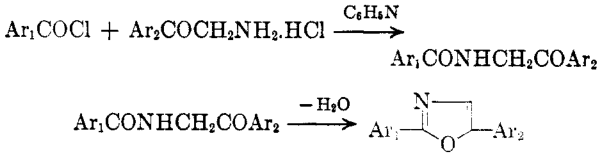
(14) R. K. Swank, W. L. Buck, F. N. Hayes, and D. G. Ott, *Rev. Sci. Instr.*, 29, 279 (1958).

The difference in the extinction coefficients of 2-(*p*-dimethylaminophenyl)-5-phenyloxazole and 5-(*p*-dimethylaminophenyl)-2-phenyloxazole could account for the difference in relative pulse heights of the two. It is thought that an increase in the extinction coefficient with the consequent diminution of the life-time of the excited state would allow fluorescence to occur before internal quenching could interfere.[9] In the case of the two isomeric dialkylamino substituted oxazoles, it can be seen that the compound with the higher pulse height is indeed the one with the larger extinction coefficient. In all cases, the extinction coefficient of the aminated oxazole is higher than that of the analogous nonaminated oxazole. Any expected improvement from this cause is offset by other, detrimental effects, as is evident in the lowered pulse heights.

It seems, in conclusion, that a molecule with an extended resonance system but with strong internal quenching or too short an emission wave length can be helped by dialkylamino substitution; however, such substitution does not improve a good scintillator.

### EXPERIMENTAL

All compounds listed in Table II were synthesized according to the following general scheme:



$$Ar_1COCl + Ar_2COCH_2NH_2.HCl \xrightarrow{C_5H_5N} Ar_1CONHCH_2COAr_2$$

The general procedure of Hayes, Rogers, and Ott[15] was used to obtain the intermediate ketoamides from the acid chlorides and the *p*-dimethylaminophenacylammonium chloride.[16]

The cyclization of the ketoamides, with 98% phosphoric acid in acetic anhydride, to form the oxazoles was performed in the same manner as that given for the pyridylphenyl oxazoles in a previous paper.[17]

Details concerning the methods for obtaining the pulse heights[18] and the fluorescence[8] and the ultraviolet absorption spectra[8] may be found in previous publications. The infrared absorption spectra are in the Sadtler Standard Spectra.[19]

Los Alamos, N. M.

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(15) F. N. Hayes, B. S. Rogers, and D. G. Ott, *J. Am. Chem. Soc.*, **77**, 1850 (1955).

(16) Product of Pilot Chemicals, Inc., Watertown, Mass.

(17) D. G. Ott, F. N. Hayes, and V. N. Kerr, *J. Am. Chem. Soc.*, **78**, 1941 (1956).

(18) F. N. Hayes, D. G. Ott, V. N. Kerr, and B. S. Rogers, *Nucleonics*, **13**, No. 12, 38 (1955).

(19) Samuel P. Sadtler and Son, Inc., Philadelphia, Pa.

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[Contribution from the Indian Association for the Cultivation of Science]

# Synthesis of Condensed Cyclic Systems. I.[1] New Synthesis of 7-Methylbicyclo[3.3.0]octan-3-one and 8-Methylbicyclo[4.3.0]nonan-4-one

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*Received April 7, 1959*

7-Methylbicyclo[3.3.0]octan-3-one (II) was obtained in good yield by application of an analogous method which had been reported for 8-methylbicyclo[4.3.0]nonan-4-one. (I). This modification, however, failed with the latter compound. A new simple method for its synthesis is described.

In the course of the synthesis of degradation products of antirachitic vitamins, Bagchi and Banerjee reported the synthesis 8-methylbicyclo[4.3.0]nonane-4-one (I).[2] The present experiments were undertaken to improve the previously developed method.

Synthesis of 7-methylbicyclo[3.3.0]octan-3-one (II) was attempted first, using simplifications of the analogous reported procedure for I. Excellent result were obtained. Fewer steps were required and a higher yield was achieved than had been reported for 8-methylbicyclo[4.3.0]nonan-4-one.

The condensation of 2-methyl-2-carbethoxylcyclopentanone with ethyl cyanoacetate according to the method of Cope *et al.*,[3] was studied by Bagchi and Banerjee.[2] In the present investigation when the condensation was carried out according to the modification of Cragoe *et al.*,[4] the condensation product (III) was obtained in a reproducible yield exceeding 90%. The unsaturated cyano ester (III) was condensed with ethyl chloroacetate according

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(1) A preliminary note embodying a part of the experimental results appeared in *Science and Culture (India)*, **21**, 545 (1956) and *Proc. 45th Session Indian Science Congress*, (1958), p. 129. Taken from the thesis of K. Sen submitted for the degree of Doctor of Philosophy (Science) of the University of Calcutta, April, 1957.

(1a) To whom all communications should be made. Present Address: Department of Chemistry, University of Maine, Orono, Me.

(2) P. Bagchi and D. K. Banerjee, *J. Indian Chem. Soc.*, **23**, 397 (1946).

(3) A. C. Cope, C. M. Hofmann, C. Wyckoff, and F. Hardenbergh, *J. Am. Chem. Soc.*, **63**, 3452 (1941).

(4) E. J. Cragoe, C. M. Robb, and J. M. Sprague, *J. Org. Chem.*, **15**, 381 (1950).