[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE AND THE BIOMEDICAL RESEARCH GROUP, LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

1,3,5-Triaryl-2-pyrazolines for Use as Scintillation Solutes

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A series of new 1,3,5-triaryl-2-pyrazolines has been synthesized for evaluation as solutes in liquid scintillation counting systems. These compounds were formed in good yields by reaction between the appropriate chalcone and arylhydrazine in glacial acetic acid at water bath temperatures. The ultraviolet and infrared spectra of these 2-pyrazolines have been analyzed. The chalcones necessary for the formation of the 1,3,5-triaryl-2-pyrazolines were formed by condensing aryl methyl ketones and aromatic aldehydes in alcohol at room temperature using alkoxide catalysis. In some cases the product isolated from such reaction mixtures was a 1,3,5-triaryl-1,5-pentanedione resulting from a Michael addition of the methyl ketone to the expected chalcone. The ultraviolet and infrared spectra of the chalcones are shown to be consistent with the *trans* configuration. The new 2-pyrazolines and some which were previously known were evaluated as solutes in liquid scintillation counting systems. The ability of this type of molecule to function as an efficient scintillator is related to aryl substitution at sites one and three and bears no resemblance to molecular types now in use.

Previous endeavors in the synthesis and evaluation of organic solutes for liquid scintillation counters have been concerned with ring systems such as terphenyl and diphenyloxazole which possess continuous conjugation.[4–13] At this time we wish to report upon the synthesis and characterization of a variety of new 1,3,5-triaryl-2-pyrazolines and the evaluation of these compounds and some previously known pyrazolines as solutes in conventional liquid scintillation counting systems.[14,15] These compounds are extremely interesting because they show considerable relative pulse height as indicated by the scintillation data in Table VI; are sufficiently soluble for practical use; and they are not appreciably self-quenching. These pyrazolines are of considerable theoretical importance because they represent the first significant departure from the usual planar, linearly conjugated systems encountered in organic scintillation solutes.

Pyrazolines are available by many synthetic approaches; however, 1,3,5-triaryl-2-pyrazolines are most conveniently available by condensation of the appropriate arylhydrazine with an α,β-unsaturated ketone homologous with chalcone (II) under acidic conditions. The generally accepted interpretation of this reaction involves the initial formation of an arylhydrazone (III) with subsequent attack of nitrogen upon the carbon-carbon double bond. Condensations involving similar systems have been run in alcoholic hydrochloric acid;[16] however, we have found that the operation is best carried out by heating equimolar quantities of the two reactants in an excess of glacial acetic acid for several hours on a steam bath. At the end of this time the product has usually begun to precipitate. The yields obtained using this procedure vary from 59% to 99% as shown in Table I.

In addition to forming pyrazolines by the method outlined above we have also observed their formation in the reaction of several 1,3,5-triaryl-1,5-pentanediones with phenylhydrazine. This preparation of triarylpyrazolines by elimination is similar to the formation of this ring system from Mannich bases[17] and β-aroyl ethanols.[18] In view of the known reversibility of Michael addition reactions it is quite probable that the formation of pyrazolines from these ketones involves a regression. In this reaction sequence the equilibrium between the triarylpentanedione and the chalcone is displaced by the formation of pyrazoline from the chalcone.

Previous studies on the ultraviolet spectra of pyrazolines have shown that when there is no substituent at position one the spectrum consists of

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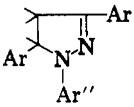
TABLE I

NEW PYRAZOLINES



Ar″	Ar′	Ar	M.P., °C.	Yield,[a] %	Analysis Nitrogen	
					Calcd.	Found
p-Biphenyl	Phenyl	*p*-Biphenyl	181–183	70, B/E	6.22	6.19
p-Biphenyl	Phenyl	Phenyl	178–178.5	73, B/E	7.48	7.45
p-Biphenyl	Phenyl	*p*-Methoxyphenyl	150–151	65, E	6.93	7.14
Phenyl	Phenyl	9-Anthryl	231–233	75, B	7.03	7.25
Phenyl	Phenyl	*p*-Biphenyl	168–169	59, T	7.48	7.70
Phenyl	2-Naphthyl	*p*-Biphenyl	231–233	61, T	6.60	6.66
Phenyl	*p*-Biphenyl	*p*-Methoxyphenyl	185	68, A	—	—[b]
Phenyl	*p*-Biphenyl	3,4-Diethoxyphenyl	165–167	76, E	6.06	5.96
Phenyl	*p*-Biphenyl	*p*-Isopropylphenyl	165.5–167	55, E	6.73	6.58
Phenyl	*p*-Biphenyl	1-Naphthyl	210	65, T/G	6.60	6.48
Phenyl	*p*-Biphenyl	*p*-Diethylaminophenyl	178–179	64, T	9.52	9.53
Phenyl	Phenyl	1-Naphthyl	173–174	[c], E	8.04	7.86
p-Carboxyphenyl	Phenyl	*p*-Methoxyphenyl	213–215	[c], E	7.52	7.25
Phenyl	*p*-Biphenyl	Phenyl	204–206	[c], E	7.48	7.75
Phenyl	*p*-Methoxyphenyl	*p*-Methoxyphenyl	147–148	[c], E	7.82	7.53
Phenyl	Phenyl	*p*-Dimethylaminophenyl	142–143	[c], E	12.31	12.51
Phenyl	*p*-Hydroxyphenyl	Phenyl	129–134	[c], E	8.91	8.60
Phenyl	Phenyl	*p*-Hydroxyphenyl	148.5–149.5	[c], E	8.91	8.95

[a] Recrystallized from A, acetone; B, benzene; E, ethanol; G, glacial acetic acid; T, toluene. [b] *Anal.* Calcd. for $C_{28}H_{24}N_2O$: C, 83.14; H, 5.98. Found: C, 83.25; H, 6.08. [c] These compounds were supplied through the generosity of the Tennessee Eastman Co., Kingsport, Tenn.

one maximum at about 240 mμ.[19] When the one position is substituted by a benzene ring a second maximum appears at about 280 mμ. This long wave length band is relatively stable except when a second benzene ring is introduced at position three, in which case the band is shifted to 354 mμ.[20] Our data, as indicated in Table II, show that the introduction of a third phenyl group at position five on the pyrazoline ring causes no alteration in this established spectral pattern. The information in this table indicates that the band at 354 mμ is relatively free of substitution effects, the greatest shifts being due to large extentions of conjugation. In contrast to the relative stability of this band the maxima at 240 mμ is extremely sensitive to substitution on any of the benzene rings. The effects produced by such alteration as noted in Table II do not appear to be predictable.

In addition to the two maxima basic to 1,3,5-triarylpyrazolines certain of these compounds show an additional band at an intermediate or longer wavelength which can be attributed to specific portions of the molecule. Thus, those materials containing *p*-methoxyphenyl substitution show a band in the 285–290 mμ region which is related to the 278-mμ band in anisole.[21] The compounds possessing *p*-dimethylaminophenyl groups show a third maxima in the 310-mμ range that is comparable to the 305-mμ band of *p*-methyl-*N*,*N*-dimethylaniline.[21] A third band also shows up in the spectrum of those compounds having either 1-naphthyl or 2-naphthyl groups on the pyrazoline ring. This band is in the 268–282 mμ region and represents the variable 270 mμ-band of the methylnaphthylenes. Similarly the 365-mμ frequency of 9-methylanthracene is found at 368 mμ in 1,3-diphenyl-5-(9-anthryl)-2-pyrazoline.

The infrared spectra of the pyrazolines were examined in the region from 6 to 16 μ; the results are recorded in Table II. Possibly the most interesting portion of the spectrum is that range around 6 μ where one would anticipate a band due to the conjugated —C=N— as well as the usual —C=C— aromatic stretching vibration. In this region, however, there is only one strong band, and this is at 6.25 to 6.3 μ. The lack of information regarding the effect of salt formation on this band makes it impossible to assign accurately its source; however, due to its strength, its origin is probably in the —C=N— bond and the associated benzene ring. If this explanation is correct the effect of conjugation on the —C=N— band is greater in pyrazolines than in those instances previously studied.[22]

The chalcones from which the 1,3,5-triarylpyrazolines were prepared were synthesized by

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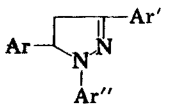
TABLE II

SPECTRAL CHARACTERISTICS OF 1,3,5-TRIARYLPYRAZOLINES

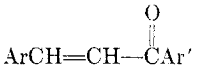


			Ultraviolet				Infrared				
Ar″	Ar′	Ar	λ_{max}[a]	log ε	λ_{max}	log ε	C=N	CH$_2$	Ar—N	—CH—N	C—H
Phenyl	Phenyl	Phenyl	242	2.24	354	4.28	6.3(vs)	7.2(s)	7.5(m)	9.0(s)	14.4(vs)
Phenyl	Phenyl	*p*-Hydroxyphenyl	229	4.41	358	4.37	6.3(vs)	7.2(s)	7.55(s)	8.9(s)	14.6(vs)
Phenyl	Phenyl	*p*-Methoxyphenyl	229	4.37	357	4.29	6.3(vs)	7.2(s)	7.55(m)	8.9(s)	14.6(vs)
Phenyl	Phenyl	*p*-Dimethylaminophenyl	254	4.42	356	4.27[b]	6.3(s)	7.2(s)	7.5(s)	8.9(s)	14.5(vs)
Phenyl	Phenyl	1-Naphthyl	224	4.92	354	4.27[c]	6.3(vs)	7.3(s)	7.6(s)	9.0(s)	14.5(vs)
Phenyl	Phenyl	*p*-Acetamidophenyl	247	4.49	355	4.27	6.3(vs)	7.2(s)	7.6(s)	8.9(s)	14.6(vs)
Phenyl	Phenyl	*p*-Biphenyl	261	4.00	373	4.46	6.3(vs)	7.2(s)	7.5(m)	8.9(s)	14.6(s)
Phenyl	Phenyl	9-Anthryl	255	5.13	353	4.40[d]	6.3(s)	7.2(s)	7.5(s)	8.9(s)	14.5(s)
Phenyl	*p*-Methoxyphenyl	Phenyl	248	4.23	352	4.33	6.3(vs)	7.2(s)	7.55(s)	9.0(s)	14.5(s)
Phenyl	2-Naphthyl	Phenyl	236	4.58	369	4.36	6.3(vs)	7.1(m)	7.6(m)	8.9(s)	14.3(s)
Phenyl	*p*-Hydroxyphenyl	Phenyl	229	4.41	358	4.37	6.3(vs)	7.2(s)	7.5(m)	9.0(s)	14.4(vs)
Phenyl	*p*-Methoxyphenyl	*p*-Methoxyphenyl	248	4.27	349	4.33	6.3(vs)	7.2(s)	7.6(m)	8.9(m)	14.5(m)
Phenyl	*p*-Biphenyl	Phenyl	262	4.37	372	4.73	—	—	—	—	—
Phenyl	*p*-Biphenyl	*p*-Methoxyphenyl	262	4.43	373	4.49	6.3(vs)	7.2(s)	7.55(m)	9.0(s)	14.6(vs)
Phenyl	*p*-Biphenyl	*p*-Isopropylphenyl	262	4.34	372	4.40	6.3(vs)	7.2(s)	7.5(m)	8.9(s)	14.55(s)
Phenyl	*p*-Biphenyl	*p*-Dimethylaminophenyl	264	4.56	377	4.42	6.3(vs)	7.2(m)	7.5(m)	9.0(s)	14.5(s)
Phenyl	*p*-Biphenyl	1-Naphthyl	225	4.83	374	4.38[e]	6.3(vs)	7.1(s)	7.55(m)	8.9(s)	14.5(vs)
Phenyl	*p*-Biphenyl	*p*-Diethylaminophenyl	264	4.46	345	4.24	6.25(vs)	7.1(m)	7.5(m)	8.8(vs)	14.5(vs)
Phenyl	*p*-Biphenyl	3,4-Diethoxyphenyl	262	4.44	373	4.50	6.3(s)	7.2(s)	7.7(m)	8.9(vs)	14.6(s)
Phenyl	2-Naphthyl	*p*-Biphenyl	241	4.25	367	4.00	6.3(vs)	7.1(s)	7.55(m)	8.9(s)	14.5(vs)
p-Biphenyl	Phenyl	Phenyl	296	4.27	367	4.55	6.3(s)	7.3(m)	7.4(w)	8.9(m)	14.5(vs)
p-Biphenyl	Phenyl	*p*-Methoxyphenyl	228	4.56	369	4.54[f]	6.25(s)	7.2(s)	7.5(m)	9.1(s)	14.5(vs)
p-Biphenyl	Phenyl	*p*-Biphenyl	252	4.45	369	4.43	6.3(vs)	7.1(s)	7.6(w)	8.8(m)	14.6(m)
p-Carboxyphenyl	Phenyl	*p*-Methoxyphenyl	229	4.39	364	4.58[g]	6.3(vs)	7.1(s)	7.6(w)	8.8(m)	14.6(m)
p-Carboxyphenyl	*p*-Methoxyphenyl	*p*-Methoxyphenyl	—	—	361	4.55	6.25(vs)	7.15(s)	7.7(vs)	9.17(m)	14.5(w)

[a] Values are expressed in mμ. [b] λ_{max}, 313 mμ; log ε, 4.00. [c] λ_{max}, 282 mμ; log ε, 4.09. [d] λ_{max}, 368 mμ; log ε, 4.41. [e] λ_{max}, 268 mμ; log ε, 4.34. [f] λ_{max}, 291 mμ; log ε, 4.32. [g] λ_{max}, 285 mμ; log ε, 4.15.

TABLE III

NEW CHALCONES



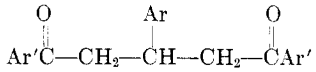
$\mathrm{ArCH{=}CH{-}\overset{O}{\overset{\|}{C}}Ar'}$

				Analysis			
				Carbon		Hydrogen	
Ar	Ar′	M.P., °C.	Yield,[a] %	Calcd.	Found	Calcd.	Found
p-Phenylene	3-bis-1(3′-pyridyl)-acrylyl[c]	233–234	85, E	—	—	—	—[b]
1-Naphthyl	2-Naphthyl	158–160	79, B	89.58	89.40	5.23	5.45
p-Diethylaminophenyl	*p*-Biphenyl	164–165	82, C	84.47	84.41	7.09	6.87
Phenyl	2-Naphthyl	106	98, E	88.34	88.05	5.46	5.52
3,4-Diethoxyphenyl	*p*-Biphenyl	147.5–149	98, E	80.62	80.54	6.50	6.52
1-Naphthyl	*p*-Biphenyl	149	67, A	89.79	89.98	5.43	5.62
p-Dimethylaminophenyl	*p*-Biphenyl	160–163	60, G/W	84.37	83.93	6.47	6.45
9-Anthryl	Phenyl	124–125	76, B	89.58	89.43	5.23	5.20
p-Biphenyl	Phenyl	111.5–112.5	72, E	88.70	88.86	5.67	5.68
p-Biphenyl	2-Naphthyl	141–142	81, B	89.79	89.81	5.43	5.62
p-Biphenyl	*p*-Biphenyl	195–197	80, B	89.97	89.73	5.59	5.67

[a] Recrystallized from A, acetone; B, benzene; C, cellosolve; E, 95% ethanol; G, glacial acetic acid; W, water. [b] *Anal.* Calcd. for $C_{22}H_{16}N_2O_2$: N, 8.23. Found: N, 8.05. [c] The chalcone from terephthalaldehyde and 3-acetopyridine.

TABLE IV

MICHAEL ADDITION PRODUCTS



$\mathrm{Ar'\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{Ar}{\overset{|}{C}}H{-}CH_2{-}\overset{O}{\overset{\|}{C}}Ar'}$

			Analysis			
			Carbon		Hydrogen	
Compound	M.P., °C.	Yield,[a] %	Calcd.	Found	Calcd.	Found
1,5-Di-(*p*-biphenyl)-3-phenyl-1,5-pentanedione	185.5–186.5	93, C	87.47	87.92	5.87	6.36
1,5-Di-(*p*-biphenyl)-3-(*p*-isopropylphenyl)-1,5-pentanedione	210	92.5, C	87.32	86.91	6.56	6.56
1,3,5-Tri-(3-pyridyl)-1,5-pentanedione	145–146	80, E/W	—	—	—	—[b]

[a] Recrystallized from C, cellosolve; E, ethanol; W, water. [b] *Anal.* Calcd. for $C_{20}H_{17}N_3O_2$: N, 12.68. Found: N, 12.56.

condensing the appropriate aromatic aldehyde and methyl ketone in alcohol at room temperature using sodium methoxide catalyst. This type of reaction is generally known to proceed through the sequence outlined in formulas I and II.[23] In those cases outlined in Table III this procedure gave high yields of the desired α,β-unsaturated ketone with no undesirable side reactions. The products precipitated from the reaction mixture in a relatively pure state and were easily recrystallized. In addition to obtaining chalcones from these aldol-type condensations it is likewise possible as shown in formulas II and IV to obtain 1,3,5-triaryl derivatives of 1,5-pentanedione resulting from Michael addition of the methyl ketone across the double bond formed in the initial condensation of aldehyde and ketone. Contrary to a previous report[24] we have observed this to occur in the condensation of benzaldehyde with *p*-phenylacetophenone as well as the other cases presented in Table IV.

The relationship between the ultraviolet spectrum and the possible structures of chalcone has been thoroughly discussed[25,26] as have the ultraviolet spectra of many simple derivatives of chalcone.[27,28] This prior work has shown that the *trans* chalcone structure has two maxima (230 mμ, log $\epsilon = 3.77$; 312 mμ, log $\epsilon = 4.38$) in the ultraviolet that are due to the planar, cross conjugated system as a whole and which generally undergo a bathochromic shift due to electron-donating substituents on either Ar or Ar′. The data in Table V show that for the more complicated structures presented here the two maxima characteristic of *trans* chalcones are usually observed and that electron donor substitution results in bathochromic shifts. The most outstanding example in this series is *p*-dimethylaminophenyl-*p*-phenylacrylophenone which has its long wave length maximum at 425 mμ (log $\epsilon = 4.53$).

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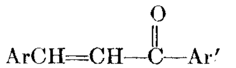
TABLE V

SPECTRAL CHARACTERISTICS OF CHALCONES



$ArCH{=}CH{-}C({=}O){-}Ar'$

		Ultraviolet				Infrared				
							Conj.	*Aormatic*		*Trans*
Ar	Ar′	λ_{max}[a]	log ε	λ_{max}	log ε	C=O	C=C	C=C	C=C	RHC=CHR
3,4-Diethoxyphenyl	Phenyl	259	4.24	357	4.35	6.2(vs)	—	6.3(s)	6.6(m)	10.2(m)
9-Anthryl	Phenyl	252	5.11	369	3.79	6.1(m)	6.18(w)	6.3(vs)	6.6(m-sh)	10.05(s)
p-Phenylene	bis-1-Phenylacrylyl	276	4.15	352	4.71[b]	6.1(s)	—	6.3(vs)	6.6(m-sh)	10.2(vs)
Phenyl	2-Naphthyl	260	4.25	312	4.44[c]	6.1(s)	6.15(w)	6.3(vs)	6.7(m)	10.2(s)
1-Naphthyl	2-Naphthyl	253	4.39	345	3.92[d]	6.1(m)	6.17(w)	6.3(vs)	6.6(m-sh)	10.2(s)
p-Biphenyl	2-Naphthyl	253	4.50	336	4.43	6.1(m)	—	6.3(vs)	6.9(m)	10.3(s)
p-Methoxyphenyl	*p*-Biphenyl	293	4.30	346	4.19[e]	6.1(s)	6.10(w)	6.3(vs)	6.7(m)	10.3(m)
p-Dimethylaminophenyl	*p*-Biphenyl	299	4.30	425	4.53[f]	6.1(m)	—	6.3(vs)	6.6(m)	10.2(m)
1-Naphthyl	*p*-Biphenyl	222	4.76	301	4.36	6.1(s)	—	6.3(vs)	6.7(m)	10.2(m)
p-Diethylaminophenyl	*p*-Biphenyl	283	4.60	390	2.90	6.03(vs)	—	6.3(s)	6.7(m)	10.45(s)
p-Biphenyl	*p*-Biphenyl	305	4.38	328	4.38	6.1(m)	6.15(w)	6.25(s)	6.7(m)	10.2(m)
3,4-Diethoxyphenyl	*p*-Biphenyl	311	4.31	361	4.38	6.1(m)	—	6.3(vs)	6.7(m)	10.3(m)

[a] Values are expressed in mμ. [b] λ_{max}, 229 mμ; log ε, 4.16. [c] λ_{max}, 220 mμ, log ε, 4.71. [d] λ_{max}, 222 mμ; log ε, 4.82; λ_{max}, 288 mμ; log ε, 4.12. [e] λ_{max}, 220 mμ; log ε, 4.19. [f] λ_{max}, 247 mμ; log ε, 4.12.

The infrared spectra of these chalcones show that the carbonyl frequencies at 6.03 μ to 6.2 μ (Table V) are displaced to a significant degree from the values reported for chalcone itself.[29,30] The band due to the conjugated —C=C— bond can be resolved in relatively few cases and then only as a weak shoulder at 6.10 μ to 6.18 μ on either the carbonyl band or the 6.3 μ band associated with the aromatic C=C bond. The two major aromatic C=C frequencies in the 6μ to 7 μ region are among the strongest observed and occur from 6.3 μ to 6.4 μ and 6.7 μ to 6.9 μ. For purposes of structure assignment the most useful portions of these infrared spectra are the 7.6 μ to 7.8 μ and 10.2 μ to 10.4 μ regions where the CH deformation frequencies characteristic of *trans* ethylenes are found. In these compounds the usefulness of the 7 μ region is diminished because the normally weak *trans* ethylenic C—H in-plane deformation frequencies are obscured by the many strong maxima from the aromatic portions of the molecules. The 10-μ region, however, is relatively free of maxima and the *trans* ethylenic C—H out-of-plane deformation frequencies are easily seen. These bands occur as medium to strong maxima from 10.0 μ to 10.45 μ and serve to identify the compounds as *trans* chalcones.

Toluene solutions of the 2-pyrazolines were subjected to conventional scintillation[9] and spectral[31] tests. The results are presented in Table I. The parameters, I_{max} and c_{max}, are the maximum relative light output and the concentration at which this occurred. The spectral quantities, λ_{max} and $\bar{\lambda}$, obtained from corrected fluorescence spectra, are the most probable wave length and the mean wave length.

The 2-pyrazoline ring will function as an inner ring in a scintillation solute molecule when aryl groups are substituted in positions 1 and 3. This bears little similarity to the usual situation in which the central ring is aromatic and substituted in a manner for simultaneous resonance interaction with the substituent groups.

1,3-Diphenyl-2-pyrazoline substituted with a variety of groups in the 5-position yields compounds whose light-producing ability is only slightly inferior to that of 2,5-diphenyloxazole. The pulse height improvement found in polyaryl scintillation solutes by lengthening the chain is not found here. A phenyl substituent is fully as good as a 4-biphenylyl substituent. A small degree of self-quenching is exhibited in this series.

Aryl groups on position 5 have little effect on I_{max} or the spectral parameters. An increase in the complexity of the aromatic systems attached to po-

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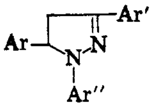
(29) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., 1954, p. 119.

(30) H. Hergert and F. Kurth, *J. Am. Chem. Soc.*, **75**, 1622 (1953).

(31) D. G. Ott, F. N. Hayes, E. Hansbury, and V. N. Kerr, *J. Am. Chem. Soc.*, **77**, 5448 (1957).

TABLE VI

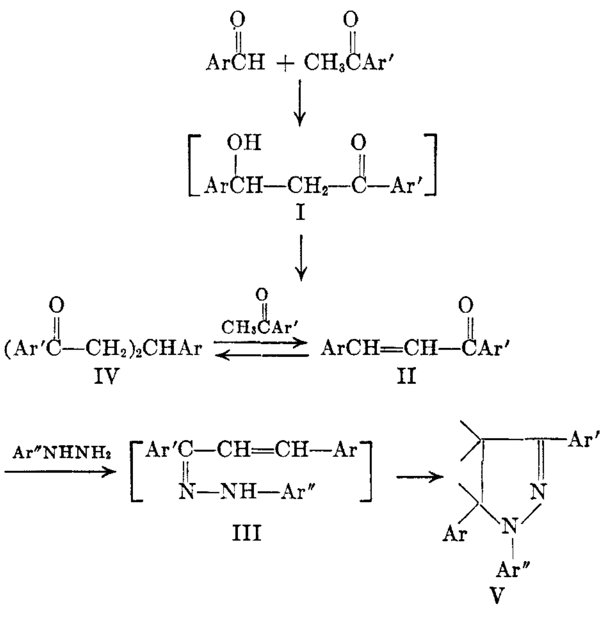
SCINTILLATION AND FLUORESCENCE DATA ON PYRAZOLINES



Solute			Scintillation Data		Fluorescence Spectral Data[a]	
Ar''	Ar'	Ar	I_{max}[b]	c_{max}', g./l.	λ_{max}, mμ	$\bar{\lambda}$, mμ
Phenyl	H	Phenyl	[c]	—	[c]	[c]
Phenyl	Methyl	Phenyl	[c]	—	[c]	[c]
Phenyl	Phenyl	Phenyl	0.88	6.5	440	460
Phenyl	Phenyl	*p*-Hydroxyphenyl	0.74	2.8	440	464
Phenyl	Phenyl	*p*-Methoxyphenyl	0.88	5.5	437	472
Phenyl	Phenyl	*p*-Dimethylaminophenyl	0.83	3.8	448	464
Phenyl	Phenyl	*p*-Acetamidophenyl	0.79	3.1[d]	442	464
Phenyl	Phenyl	1-Naphthyl	0.30	5.8	437	468
Phenyl	Phenyl	*p*-Biphenyl	0.77	4.6	444	464
Phenyl	Phenyl	9-Anthryl	[c]	—	[c]	[c]
Phenyl	*p*-Hydroxyphenyl	Phenyl	0.63	2.3	432	472
Phenyl	*p*-Methoxyphenyl	Phenyl	0.90	5.8	436	440
Phenyl	*p*-Methoxyphenyl	*p*-Methoxyphenyl	0.85	4.9	436	456
Phenyl	2-Naphthyl	Phenyl	0.58	2.0	458	480
Phenyl	2-Naphthyl	*p*-Biphenyl	0.62	1.4[d]	456	476
Phenyl	*p*-Biphenyl	Phenyl	0.86	5.2	458	480
Phenyl	*p*-Biphenyl	*p*-Isopropylphenyl	0.79	6.0	462	482
Phenyl	*p*-Biphenyl	*p*-Methoxyphenyl	0.81	5.3	462	482
Phenyl	*p*-Biphenyl	3,4-Diethoxyphenyl	0.82	5.5	461	484
Phenyl	*p*-Biphenyl	*p*-Dimethylaminophenyl	0.78	5.4	466	484
Phenyl	*p*-Biphenyl	1-Naphthyl	0.78	5.2	460	480
p-Carboxyphenyl	Phenyl	*p*-Methoxyphenyl	0.78	3.0[d]	432	448
p-Carboxyphenyl	*p*-Methoxyphenyl	*p*-Methoxyphenyl	[c]	—	432	452
p-Biphenyl	Phenyl	Phenyl	0.76	5.6	459	476
p-Biphenyl	Phenyl	*p*-Methoxyphenyl	0.64	3.1	458	476
p-Biphenyl	Phenyl	*p*-Biphenyl	0.74	5.4	458	484
5,5'-*p*-Phenylenebis(1,3-diphenyl-2-pyrazoline)			0.09	1.3[d]	446	464

[a] 314 mμ Hg-arc line excitation. [b] Measured relative to 3 g./l. 2,5-diphenyloxazole, as pulse heights[9] with a Ba^{137} electron source, an evaporated aluminum reflector and a photomultiplier having average S-11 spectral characteristics. [c] Response too weak for measurement. [d] Concentration of saturated solution.

sitions 1 and 3 gives larger values of λ_{max} and $\bar{\lambda}$, but does not increase I_{max}.



EXPERIMENTAL[32]

The *p*-phenylacetophenone, substituted benzaldehydes, acetonaphthones, and 9-anthraldehyde were obtained from commercial sources. The 4-biphenylcarboxaldehyde[33] and 4-biphenylhydrazine[34] were prepared by previously described procedures. Typical procedures for the preparation of the various products obtained are given in the following paragraphs. Details of the other preparations are given in Tables I, III, and IV.

4,4'-Diphenylchalcone. A solution of 3.64 g. of 4-biphenylcarboxaldehyde and 3.92 g. of *p*-phenylacetophenone in 130 ml. of 95% ethanol was mixed with 4 ml. of 20% sodium methylate in methanol and allowed to stand for 20 hr. at room temperature. The crystalline precipitate was filtered, washed with 95% ethanol, and recrystallized twice from benzene to give 5.74 g. (80%) of pale yellow crystals, m.p. 195–197°.

Anal. Calcd. for $C_{27}H_{20}O$: C, 89.97; H, 5.59. Found: C, 89.81; H, 5.62.

1,5-Di(p-biphenyl)-3-phenyl-2-pyrazoline. A solution of 0.71 g. of 4-phenylchalcone and 0.46 g. of 4-biphenylhydrazine in 15 ml. glacial acetic acid was heated on a water bath at 100° for 2 hr. After 0.5 hr. crystallization commenced and was complete upon standing at room tempera-

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(32) Analyses by Micro Tech Laboratories, Skokie, Ill.

(33) D. H. Hey, *J. Chem. Soc.*, 2476 (1931).

(34) H. Müller, *Ber.*, **27,** 3105 (1894).

ture for 14 hr. The product was filtered, washed with 95% ethanol, and recrystallized from a mixture of benzene and 95% ethanol to give 0.79 g. (70%) of yellow crystals, m.p. 180–183°.

Anal. Calcd. for $C_{33}H_{26}N_2$: N, 6.22. Found: N, 6.19.

1,5-Di(p-biphenyl)-3-(p-isopropylphenyl)-1,5-pentanedione. A 75% solution of sodium ethoxide in 95% ethanol was added to a mixture of 3.0 g. of *p*-isopropylbenzaldehyde and 4.0 g. of *p*-phenylacetophenone in 75 ml. of 95% ethanol. After standing for 24 hr. the crude product was filtered, washed with water, and recrystallized from Cellosolve to give 4.2 g. (80.6%) of white needles, m.p. 210°.

Anal. Calcd. for $C_{33}H_{34}O_2$: C, 87.32; H, 6.56. Found: C, 86.91; H, 6.56.

1-Phenyl-3-(p-biphenyl)-5-(p-isopropylphenyl)-2-pyrazoline. A solution of 5.0 g. of 1,5-di(*p*-biphenyl)-3-(*p*-isopropylphenyl)-1,5-pentanedione and 1.1 g. of phenylhydrazine in 25 ml. of glacial acetic acid was heated at 80° for 2 hr. After cooling to room temperature the product was filtered, washed with water, and recrystallized once from benzene and twice from 95% ethanol to give 1.2 g. (55%) of yellow plates, m.p. 167°.

Anal. Calcd. for $C_{30}H_{28}N_2$: N, 6.73. Found: N, 6.58.

Ultraviolet and infrared absorption data. The ultraviolet absorption measurements were made with Beckman DU and DK-2 spectrophotometers using 1.00-cm. silica cells and hydrogen discharge light sources. Absolute methanol solutions were used. The infrared spectral measurements were made with a Baird double beam recording spectrometer using potassium bromide pellets.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

1,1-Diethoxy-3-(triphenylstannyl)-2-propyne

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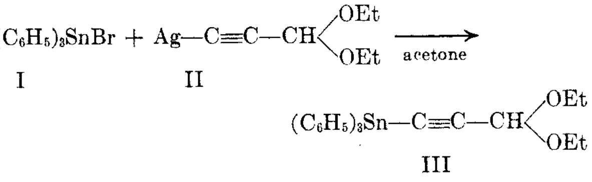
The synthesis and properties of an acetylenic tin compound containing a potential aldehyde group are presented.

The only organotin derivatives of acetylene, bis(triphenyltin)acetylene and bis(triethyltin)acetylene, found in the literature were reported by Beermann and Hartmann.[3] These two acetylenic tin compounds were found to have weak tin-carbon bonds. The ethyl derivative slowly hydrolyzed to triethyltin hydroxide and acetylene. Both reacted readily with base forming triorganotin hydroxides and acetylene. Acids also split the tin-carbon bond. In the presence of silver ion or ammoniacal copper(I) ion, silver or copper(I) acetylide formed. Iodine also broke the tin-carbon bond. Ethylmagnesium bromide reacted with bis(triphenyltin)acetylene to form ethyltriphenyltin and acetylenedimagnesium bromide. The stability of both the trialkyl or triaryltin cation and the acetylenic anion contributed greatly to the ease of cleavage of the tin-carbon bonds in these cases.

We have prepared an acetylenic organotin compound containing a potential aldehyde group and have found that the tin-carbon bond wherein the carbon atom is part of an acetylenic linkage is indeed very readily broken. 1,1-Diethoxy-3-(triphenylstannyl)-2-propyne, III, was prepared by the action of the silver salt of propiolaldehyde diethylacetal, II, on triphenyltin bromide, I,



$$\underset{\text{I}}{(C_6H_5)_3SnBr} + \underset{\text{II}}{Ag{-}C{\equiv}C{-}CH\begin{smallmatrix}OEt\\OEt\end{smallmatrix}} \xrightarrow[\text{acetone}]{} \underset{\text{III}}{(C_6H_5)_3Sn{-}C{\equiv}C{-}CH\begin{smallmatrix}OEt\\OEt\end{smallmatrix}}$$

The structure of 1,1-diethoxy-3-(triphenylstannyl)-2-propyne was assigned primarily on the basis of origin and analytical data. Its infrared spectrum in chloroform did not show absorption in the region 2000-2400 cm^{-1} but this does not rule out the possible existence of a disubstituted acetylene.[4] The chemical behavior indicated a very weak tin-carbon bond. Action of dilute hydrochloric acid (1%) gave triphenyltin chloride. Dilute alkali reacted with 1,1-diethoxy-3-(triphenylstannyl)-2-propyne to give triphenyltin hydroxide. The search for other products was not fruitful. Attempts to prepare a 2,4-dinitrophenylhydrazone of 1,1-diethoxy-3-(triphenylstannyl)-2 propyne by *in situ* hydrolysis of the acetal linkage was unsuccessful and a control experiment with

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(2) Supported by a Grant-in-Aid of Research from the Graduate School of the University of Minnesota. Present address: Department of Chemistry, Augsburg College, Minneapolis 6, Minnesota.

(3) C. Beermann and H. Hartmann, *Z. anorg. Chem.*, **276**, 20 (1954).

(4) L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Methuen & Co. Ltd., London, 1954, pp. 48–53.