spectrum showed only one proton signal, the compound was considered to be 4-chloro-2,6-diazidonitrobenzene.

Identification of 5-Chloro-2,4-diazidonitrobenzene. To determine the location of the azide group, this compound (0.3 gram) was dissolved in 35 ml. of 2-methoxyethanol, and cooled to 0°C. A solution of 6 grams of arsenic trioxide (*11*) and 16 grams of potassium hydroxide in 15 ml. of a 50% aqueous solution of 2-methoxyethanol was added dropwise with stirring. The reaction mixture was then quenched in ice water. The crystals which formed melted at 189–90° C. The infrared spectrum indicated the presence of amine and nitro groups, and the melting point was the same as that found by Morgan and Wooton (*7*) for 5-chloro-2,4-diaminonitrobenzene.

In the reaction of 2,4,6-trichloronitrobenzene with azide ion in DMSO, the two chlorines ortho to the nitro group are replaced, while in the reaction with pentachloronitrobenzene, which also has two chlorines ortho to a nitro group, the nitro group is replaced with an azide group. The first reaction is similar to the reaction of 2,4,6-trichloronitrobenzene with methoxide ion to form 2-methoxy-4,6-dichloronitrobenzene (*4*). This type of reaction is explained by Hammond and Hawthorne (*3*) by assuming that the nitro group, originally in a noncoplanar conformation, may sandwich itself between the chlorine and the azide group in the transition state, thereby assuming an essentially coplanar conformation, and causing an increase in the resonance energy. In the case of pentachloronitrobenzene, apparently the combined inductive effects of the five chlorines is the dominant factor in causing the nitro group to be displaced by the azide ion.

Reactions of o- and p-Azidonitrobenzenes , 3, 5-Dinitroazidobenzene, and 5-Chloro-2,4-diazidonitrobenzene with Benzyne. The reactions with the first three of these compounds were carried out by refluxing a mixture of 0.05 mole of the azide and 6 grams (0.058 mole) of *n*-butyl nitrite in 200 ml of dichloromethane, and adding dropwise a solution of 7 grams (0.051 mole) of anthranilic acid in 60 ml. of acetone. The reaction mixture was evaporated to about one fourth of the original volume and this mixture was chromatographed through a column of alumina. The column was eluted with dichloromethane, the eluates evaporated to dryness, and the resulting residues recrystallized.

The 1-(4-nitrophenyl)-benzotriazole (*8*) was recrystallized from DMSO and melted at 239°C. The 1-(2-nitrophenyl)-benzotriazole (*10*) was recrystallized from benzene-cyclohexane and melted at 117–18° C. The 1-(3,5-dinitrophenyl)-benzotriazole was recrystallized from chloroform petroleum ether and melted at 169–9.5° C.

Anal. Calcd. for $C_{12}H_7N_5O_4$: C, 50.53; H, 2.46; N, 24.56. Found: C, 50.66; H, 2.58; N, 24.45.

In the reaction with 5-chloro-2,4-diazidonitrobenzene, 1.2 grams (0.005 mole) of this compound and 1.2 grams (0.012 mole) of *n*-butyl nitrite were dissolved in 50 ml. of dichloromethane at room temperature. A solution of 1.4 grams (0.01 mole) of anthranilic acid in 15 ml. of acetone was added dropwise over a period of 30 minutes. Evaporation of the solvents left a thick black oil, which was chromatographed on alumina. Elution with dichloromethane gave an oil which was crystallized from absolute ethanol; yield, 0.73 gram. After several recrystallizations from chloroform–petroleum ether, an analytical sample was obtained, m.p. 195–6° C. Anal. Calcd. for $C_{12}H_6ClN_7O_2$: C, 45.64; H, 1.90; N, 31.06. Found: C, 45.69; H, 2.07; N, 31.16. The infrared spectrum of the product in methylene chloride showed absorption bands at 2120 (N_3), 1580 (N=N), 1545 and 1340 cm.$^{-1}$ (NO_2). The product was identified as either 1-(5-azido-2-chloro-4-nitrophenyl)-benzotriazole or 1-(5-azido-4-chloro-2-nitrophenyl)-benzotriazole.

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3,3′-Keto Biscoumarins

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The Knoevenagel synthesis of 3,3′-keto biscoumarins has been expanded and several new related compounds have been produced. The properties of the compounds have been examined; the spectral characteristics, including fluorescence, have been determined and the 2,4-dinitrophenyl hydrazone derivatives prepared.

SOME YEARS AGO Knoevenagel and Langensiepen (*2*) were able to synthesize 3,3′-keto biscoumarin, designated by them as di[coumarinyl-(3)]ketone. An examination of their publication showed this to be the only compound of its nature produced by them and a search of the literature failed to reveal the existence of any other generically related compounds. The compounds described in this report were all prepared by essentially the same conditions as those employed by Langensiepen.

When the reaction was tried with 2,4,6-trihydroxybenzaldehyde, *o*-vanillin, gentisaldehyde, and 3,5-dibromosalicylaldehyde, water-imbibing compounds were obtained

Table I. 3,3′-Keto Biscoumarins

No.[a]	Aldehyde Used	M.P.,[b] °C.	Yield, %	Formula	Calculated C	Calculated H	Calculated N	Calculated Hal	Found C	Found H	Found N	Found Hal
I	Salicylaldehyde	249.5[c] 250	82	$C_{19}H_{10}O_5$	71.69	3.16			71.59	3.34		
II	5-Nitro salicylaldehyde	dec. >147	89	$C_{19}H_8N_2O_9$	56.44	1.99	6.43		56.14	2.43	6.10	
III	5-Chloro salicylaldehyde	dec. >163	43	$C_{19}H_8Cl_2O_5$	58.94	2.08		18.31	58.59	2.34		18.08
IV	5-Bromo salicylaldehyde	dec. 138–139	78	$C_{19}H_8Br_2O_5$	47.97	1.69		33.57	47.78	1.76		33.84
V	2,4-Dihydroxy benzaldehyde	>360	97	$C_{19}H_{10}O_7 \cdot H_2O$	61.98	3.28			62.20	3.61		

[a] I = 3,3′-Keto biscoumarin; II = 6,6′-dinitro-3,3′-keto biscoumarin; III = 6,6′-dichloro-3,3′-keto biscoumarin; IV = 6,6′-dibromo-3,3′-keto biscoumarin; V = 7,7′-dihydroxy-3,3′-keto biscoumarin. [b] All melting points were taken in duplicate on paired Fisher-Johns melting blocks. [c] Lit. (2) m.p. 236°; however, when sample prepared as described and recrystallized twice from acetic acid m.p. same as given above.

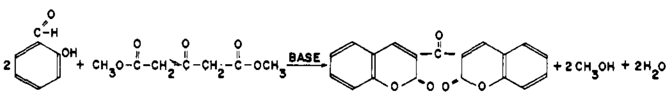
Table II. Spectral Characteristics and 2,4-Dinitrophenylhydrazones of I-V Series

				2,4-Dinitrophenylhydrazones			
						Nitrogen	
No.	Fluorescence in QRS[a]	Infrared Absorption[b] Maxima in Range of 1800 to 1500 Cm.⁻¹	Ultraviolet Maxima Range 200 to 400 Mμ[c]	Formula	M.P.,[d] °C.	Calcd.	Found
I	0.002	1715; 1650; 1600; 1550	307.5	$C_{25}H_{14}N_4O_8$	265.5–6.5	11.24	11.14
II	0.123	1723; 1603; 1503	271	$C_{25}H_{12}N_6O_{12}$	166 dec.	14.28	14.04
III	1.63	1720; 1600	274	$C_{25}H_{12}Cl_2N_4O_8$	279–81	9.87	9.62
IV	0.309	1733; 1658; 1609	228; 302; 352	. . .	. . .	. . .	. . .
V	530.00	1718; 1685; 1600; 1551	381	$C_{25}H_{14}N_4O_{10}$	>300	10.56	10.39

[a] QRS-Quinine reference units. For any value >1 the substance is a stronger blue fluorescer than quinine sulfate expressed in quantitative terms (*4*). [b] Infrared spectra taken on Beckman IR-8 using KBr pellets. [c] Ultraviolet measurements taken on Beckman Model DB-G in spectrograde methanol. [d] All melting points were taken in duplicate on paired Fisher-Johns melting blocks.

which were highly colored and tacky. The thoroughly dried substances had very high decomposition points and were of uncertain purity. The compounds described are, therefore, only those which gave good results as to yields and ease of handling.

The purpose of this study was to ascertain if such symmetrical compounds had any properties peculiar to their special structure. For this purpose compound I, the simplest member of the I-V series, was selected as a model.



I

The reaction for the preparation of compound I is given above and may be considered to be the general course of the reaction for the preparation of the other members of the series presented in Table I.

Compound I was thermochromic, as were other members of the series. The compound's NMR spectrum was very simple, giving a single peak at 7.46 p.p.m. (δ) in $CDCl_3$, indicating the proper number and equivalence of all hydrogens in the compound.

The failure of the ketone carbonyl to be reduced under Clemmensen conditions was probably due to complex formation. Dilute alcohol solutions of compound I and zinc acetate produced a precipitate which upon ignition gave ash that contained zinc.

Since coumarins usually, but not always, give several maxima in their ultraviolet spectra (*3*) in the range of 200 to 400 mμ, it was surprising to find that all compounds described here gave a single maxima (Table II) except compound IV. Further, coumarins having electrophilic groups in position 3 are likely to exhibit fluorescence (*1*), and interestingly all of the members of the series exhibited at least a measurable amount of fluorescence. The phenomenon was pronounced in compound II and extremely so in compound V. Data are given in Table II on the optical characteristics of the I-V series and their 2,4-dinitrophenyl hydrazones are described. The 2,4-dinitrophenyl hydrazone of compound IV consistently failed to give expected nitrogen and bromine values.

EXPERIMENTAL

Preparation of Compounds of I-V Series. Mixtures consisting of 0.05 mole of dimethyl acetonedicarboxylate, 0.1 mole of the aldehyde, 100 ml. of benzene, and 10 ml. of piperidine were thoroughly shaken and then warmed at 80° C. for 30 minutes. The mixtures were then poured into crystallizing dishes and 100 ml. of 6*N* hydrochloric acid was added. The benzene was allowed to evaporate in air, and the residues were filtered off and dried in air to give the crude yields recorded in Table I.

The substances, except compound III, were purified by extracting the material with hot tetrahydrofuran, filtering, and precipitating from the filtrate with heptane. The process was repeated for a second or third recrystallization.

Compound III was taken up in ethyl acetate and filtered and the substance precipitated with heptane. This operation was repeated for a second recrystallization.

The 2,4-dinitrophenyl hydrazones were prepared in the usual manner but since they were insoluble in hot ethanol they were taken up in tetrahydrofuran and precipitated with ice-cold absolute ethanol.

ACKNOWLEDGMENT

All analyses were made by Carl Tiedcke, 705 George St., Teaneck, N. J.

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CORRECTION

In the article "Graphical Determination of Virial Coefficients by the Burnett Method. Isopentane and Neopentane" by I. H. Silberberg, David C. K. Lin, and J. J. McKetta [J. CHEM. ENG. DATA **12**, 226 (1967)], the temperature data were not included for Table III on page 231. Runs 2 to 17, inclusive, were at 100° C.; runs 18 to 21, inclusive, were at 200° C.

CORRECTION

In the article "Activity of Sodium in Sodium Amalgams from E.M.F. Measurements" by M. L. Iverson and H. L. Recht [J. CHEM. ENG. DATA **12**, 262 (1967)], X_{Na} was omitted from the second term of the right hand side of Equation 5 on page 264. The correct equation is:

$$\log \gamma_{Na} = \frac{-8387.6}{T^{1.138}} + \frac{338.2}{T^{0.54}} X_{Na} + 7.0\, X^2_{Na} \qquad (5)$$