Absorption Spectra of Nitro- and Fluoro-derivatives of Phenanthrene, Triphenylene, and Pyrene.

By P. M. G. Bavin and M. J. S. Dewar.

[Reprint Order No. 6654.]

During experiments to provide quantitative data on reactivity in aromatic substitution reactions we synthesised all the mononitro-derivatives of phenanthrene and triphenylene (Bavin and Dewar, *J.*, 1955, 4479). Professor H. C. Longuet-Higgins asked us to prepare, from the available amines *via* the diazonium fluoroborates, the corresponding fluoro-compounds and determine their absorption spectra, for comparison with a general theory of substituent effects on light absorption which he and Mr. J. N. Murrell had developed. The Table records the spectra [wavelengths of absorption maxima in mμ, intensites (in parentheses) as $\log_{10} \varepsilon_{\text{max.}}$] of the fluoro- and mononitro-derivatives and also of 1-nitro- and 1-fluoro-pyrene. As the spectra of the nitro- and fluoro-benzenes and -naphthalenes are known, these results provide a good range of comparable data for the testing of theories of light absorption. For complete spectra see Bavin (Ph.D. Thesis, London, 1954).

Fluorophenanthrenes.

1-	2-	3-	4-	9-
246 (4·67)	—	—	—	—
253·5 (4·78)	250 (4·82)	249·5 (4·77)	247·5 (4·96)	248—250 (4·73)
—	265·5 (4·18)	269 (4·19)	267·5 (4·04)	269 (4·15)
275 (4·08)	275·5 (4·15)	274·5 (4·20)	274 (4·03)	275 (4·11)
283·5 (4·02)	282 (4·04)	280·5 (4·06)	285 (4·11)	284·5 (3·95)
295·5 (4·17)	294 (4·09)	292·5 (4·05)	296·5 (4·27)	296·5 (4·01)
317·5 (2·72)	315 (2·56)	318 (2·79)	318 (2·70)	317·5 (2·62)
326 (2·62)	322 (2·44)	325·5 (2·68)	326 (2·66)	325 (2·54)
332·5 (3·04)	330 (2·65)	333·5 (3·04)	332 (3·04)	332·5 (2·85)
341·5 (2·61)	337 (2·35)	341·5 (2·65)	341·5 (2·64)	340·5 (2·54)
348·5 (3·14)	346 (2·49)	349·5 (3·16)	348 (3·11)	348·5 (2·93)

Nitrophenanthrenes.

1-	2-	3-	4-	9-
240 (4·71)	238·5 (4·15)	245 (4·84)	221 (4·37)	248·5 (4·66)
298·5 (3·98)	267·5 (4·63)	262 (4·67)	240 (4·62)	290 (3·98)
	276 (4·67)	266 (4·65)	278 (4·09)	332 (3·82)
	292 (4·26)	295·5 (3·90)	298·5 (3·98)	
	312 (4·10)	335 (4·03)		
	361 (3·15)			

Fluorotriphenylenes.		*Nitrotriphenylenes.*		1-*Fluoropyrene*	1-*Nitropyrene.*
1-	2-	1-	2-	232 (4·61)	233 (4·61)
252 (5·01)	249 (4·95)	243 (5·46)	243·5 (5·12)	241 (4·88)	285 (4·18)
259·5 (5·18)	258 (5·18)	244 (5·46)	251·5—2 (5·08)	252·5 (4·06)	313 (3·70)
274·5 (4·33)	273 (4·26)	—	274·5 (5·04)	263 (4·37)	—
287 (4·29)	284 (4·20)	249 (5·51)	309·5 (4·40)	273·5 (4·66)	372—3 (4·12)
—	304 (3·42)	255 (5·54)	334·5 (4·36)	307·5 (4·01)	—
316·5 (2·83)	314·5 (2·88)			321 (4·39)	392 (4·07)
324·5 (2·69)	321·5 (2·77)			338 (4·57)	—
331 (3·00)	329·5 (2·95)			356 (3·32)	408 (3·99)
338·5 (2·60)	336·5 (2·72)			367·5 (2·87)	
347 (2·93)	345 (2·95)			375 (3·48)	

Experimental.—The diazonium fluoroborates were refluxed in light petroleum (b. p. 100—120°) for 30 min. By chromatography in light petroleum on alumina, followed by sublimation *in vacuo* and recrystallisation, were obtained in good yield : 1-*fluorophenanthrene*, blades, m. p. 100° (from light petroleum) (Found : C, 85·9; H, 4·9. $C_{14}H_9F$ requires C, 85·6; H, 4·6%); 2-*fluorophenanthrene*, plates, m. p. 104—105° (from light petroleum or methanol) (Found : C, 86·0; H, 4·8%); 3-*fluorophenanthrene*, plates, m. p. 84° (from methanol) (Found : C, 85·7; H, 4·8%); 4-*fluorophenanthrene*, white needles, m. p. 47° (from methanol) (Found : C, 86·0; H, 4·7%); 9-fluorophenanthrene, prisms, m. p. 51·2° (lit., 51—52°) (from light petroleum), and 1-*fluoropyrene*, long white needles (m. p. 136°) (from light petroleum) (Found : C, 87·9; H, 4·4.

$C_{16}H_9F$ requires C, 87·3; H, 4·1%). The *picrate* of the last crystallised from ethanol or acetic acid in blood-red needles, m. p. 208—210° (Found : N, 9·45. $C_{22}H_{12}O_7N_3F$ requires N, 9·35%).

We thank the University of London for a research grant; one of us (P. M. G. B.) gratefully acknowledges a maintenance grant by the Department of Scientific and Industrial Research.

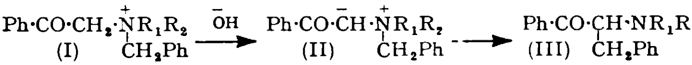
QUEEN MARY COLLEGE, UNIVERSITY OF LONDON. [*Received, July 28th*, 1955.]

The Degradation of Quaternary Ammonium Salts. Part IX. Demonstration of the Strictly Intramolecular Character of a Rearrangement.*

By R. A. W. JOHNSTONE and T. S. STEVENS.

[Reprint Order No. 6601.]

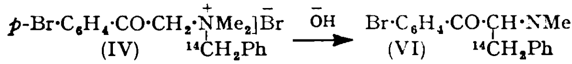
THE rearrangement (Stevens *et al.*, *J.*, 1928, 3193; 1930, 2107) of dialkylbenzylphenacylammonium bromides (I) to α-dialkylamino-ketones (III) seems to proceed *via* an intermediate zwitterion (II).



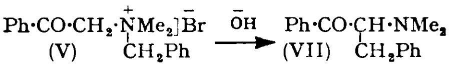
$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\underset{CH_2Ph}{\overset{+}{N}}R_1R_2}\ \text{(I)} \xrightarrow{\bar{O}H} \mathrm{Ph{\cdot}CO{\cdot}\bar{C}H{\cdot}\underset{CH_2Ph}{\overset{+}{N}}R_1R_2}\ \text{(II)} \dashrightarrow \mathrm{Ph{\cdot}CO{\cdot}\underset{CH_2Ph}{C}H{\cdot}NR_1R_2}\ \text{(III)}$$

In the rearrangement of a mixture of two quaternary salts no interchange of migrating groups could be detected, but this demonstration of the intramolecular character of the change was incomplete, since barely 80% of the initial material consumed was accounted for. Hauser and Kantor (*J. Amer. Chem. Soc.*, 1951, **73**, 1437) likewise concluded that the reaction was intramolecular and that the migrating radical did not migrate as an ion. This was largely confirmed by the observation (Campbell, Houston, and Kenyon, *J.*, 1947, 93; Brewster and Kline, *J. Amer. Chem. Soc.*, 1952, **74**, 5179) that optically active dimethylphenacyl-1-phenylethylammonium bromide is rearranged with 97% retention of the configuration of the active centre. The American authors inferred that the reaction was an intramolecular type of nucleophilic displacement and that the radical did not move as an ion. The same data are accommodated by Dewar's description (*Ann. Reports*, 1951, **48**, 127; *Bull. Soc. chim. France*, 1951, C71) of the reaction in terms of the molecular-orbital π-complex theory as involving the migration of a positively charged radical which does not escape from the molecule at any time.

Very complete evidence for the intramolecular nature of the reaction has now been obtained by the use of benzyl-*p*-bromophenacyldimethylammonium bromide (IV) in which the migrating benzyl group is radioactively labelled with ^{14}C. A mixture of this compound with benzyldimethylphenacylammonium bromide (V) whose rates of rearrangement are in the ratio 0·8 : 1 (Thomson and Stevens, *J.*, 1932, 55) was treated with alkali.



$$p\text{-}\mathrm{Br{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}\underset{^{14}CH_2Ph}{\overset{+}{N}}Me_2]\bar{B}r}\ \text{(IV)} \xrightarrow{\bar{O}H} \mathrm{Br{\cdot}C_6H_4{\cdot}CO{\cdot}\underset{^{14}CH_2Ph}{C}H{\cdot}NMe_2}\ \text{(VI)}$$



$$\mathrm{Ph{\cdot}CO{\cdot}CH_2{\cdot}\underset{CH_2Ph}{\overset{+}{N}}Me_2]\bar{B}r}\ \text{(V)} \xrightarrow{\bar{O}H} \mathrm{Ph{\cdot}CO{\cdot}\underset{CH_2Ph}{C}H{\cdot}NMe_2}\ \text{(VII)}$$

The tertiary amines (VI) and (VII) were separated and no radioactivity appeared in (VII), showing that there had been no interchange of migrating groups.

In the synthesis of the bromide (IV), radioactive formaldehyde was used to chloromethylate benzene (Blanc, *Bull. Soc. chim. France*, 1923, **33**, 313) and the resulting benzyl chloride converted successively into benzyldimethylamine and (IV) On the small scale, conditions for obtaining good yields in the chloromethylation were critical.

Experimental.—A solution of the salts (IV) and (V) (200 mg. of each) in a slight excess of 0·1N-sodium ethoxide was kept at 50° for 48 hr. (ample time for complete reaction). Water

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* Part VIII, *J.*, 1934, 279.

was added and the precipitated bases were extracted with ether. The combined ethereal extracts were treated with 2N-sulphuric acid (5 ml.), and the acid solution was heated to about 50°. 10N-Hydrochloric acid (10 ml.) was added and the solution left to cool in ice. Most of the hydrochloride of the base (VI) separated together with a little of that of (VII). The free base (VI), crystallised from ethanol, melted at 104°, alone or mixed with a non-radioactive specimen. The remaining acid solution was made basic and the precipitated base (VII) was recrystallised three times from ethanol [to ensure the absence of radioactive contamination by small amounts of (VI)]; its m. p., 77—78°, was not depressed by admixture with an authentic specimen.

Samples of the compounds (IV), (VI), and VII) were matted on small metal planchettes. The degree of radioactivity in each sample was measured, at infinite thickness, by a Geiger-Müller end-window counter, giving the following results :

Sample	None	(IV)	(VI)	(VII)
Counts min.^{-1} cm.^{-2}	16	373	403	13

Preparation of benzyl chloride. The following conditions gave the best results. Paraformaldehyde (100 mg., containing 3·7 mg. of radioactive formaldehyde), water (0·24 ml.), anhydrous zinc chloride (450 mg.), and benzene (2 ml.) were placed in a test-tube (15 × 2 cm.) and kept at 65°. A rapid stream of dry hydrogen chloride was passed in for 20 min., through a narrow glass tube so that there was efficient mixing. The product was extracted with ether, dried (Na_2SO_4), and distilled, giving fractions (i) bath 110°/20 mm., benzyl chloride (200 mg., 47%), and (ii) bath 170°/20 mm., ωω'-dichloro-*p*-xylene. Much poorer yields were obtained when no water was used in the reaction.

Benzyldimethylamine was prepared by adding benzyl chloride (200 mg.) to a saturated ethanolic solution of dimethylamine (20 ml.). After 24 hr. the solution was refluxed for a few minutes to remove excess of dimethylamine, diluted with water, and extracted with ether. After drying of the extract (Na_2SO_4), benzyldimethylamine was distilled (bath 115°/20 mm.; 150 mg., 70%).

Benzyl-*p*-bromophenacyldimethylammonium bromide (IV) was obtained by mixing *p*-bromophenacyl bromide (400 mg.) and benzyldimethylamine (150 mg.) in dry benzene. After 18 hr. the white precipitate was centrifuged and washed with dry benzene. Recrystallised from ethanol-ether it had m. p. 186—187°, alone or mixed with a non-radioactive specimen. The compounds (IV—VII) are described by Stevens *et al.* (*loc. cit.*).

We thank the University of Sheffield for a Henry Ellison Fellowship (to R. A. W. J.).

THE UNIVERSITY, SHEFFIELD. [*Received, July 12th,* 1955.]

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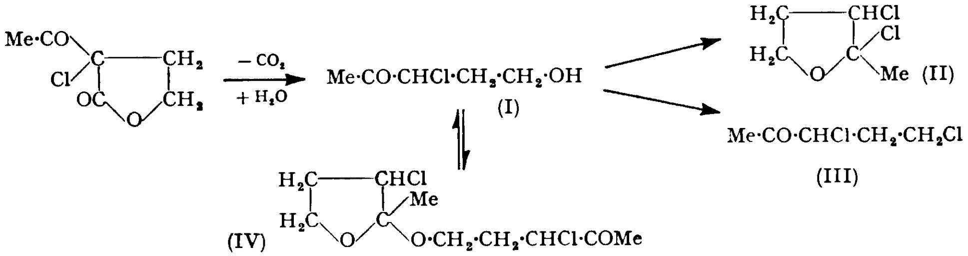
3 : 5-*Dichloropentan*-2-*one*.

By L. CROMBIE, S. H. HARPER, and B. J. STOKES.

[Reprint Order No. 6638.]

ACCORDING to patent literature (Kerestzy and Wolf, B.P. 609,803, 615,404; Konig, Gerecs, and Foldi, U.S.P. 2,393,109) 2 : 3-dichlorotetrahydro-2-methylfuran (II) may be conveniently prepared from acetylchlorobutyrolactone (Buchman, *J. Amer. Chem. Soc.*, 1936, **58**, 1803) by decarboxylation and treatment with hydrogen chloride. Stevens and Stein (*ibid.*, 1940, **62**, 1045) have shown that the main product from decarboxylation of acetylchlorobutyrolactone is the tetrahydro-2-furyl ether (IV), some 3-chloro-4-oxopentanol, (I) and, perhaps, its cyclic oxide form also being formed. It is presumably this observation which has led Kerestzy and Wolf to formulate their product as (II).

We find that the product from the above reaction, whilst having a reasonable analysis for the tetrahydrofuran (II) differs widely in physical constants from those reported by Paul and Tchelitcheff (*Bull. Soc. chim.*, 1950, **17**, 520) for 2 : 3-dichlorotetrahydro-2-methylfuran prepared by addition of chlorine to 4 : 5-dihydro-2-methylfuran. Furthermore, its infrared spectrum shows a strong band at 1725 $cm.^{-1}$ consistent with an α-chloroketone structure, together with a weaker one at 1773 $cm.^{-1}$ which may be due to lactone contaminant. It gives a 2 : 4-dinitrophenylhydrazone. A positive iodoform test and colour reactions also support the methyl ketone structure (III). Authentic 2 : 3-dichlorotetrahydro-2-methylfuran (II) (Paul and Tchelitcheff, *loc. cit.*) reacts readily with alkylmagnesium halides to yield 2 : 2′-dialkyl-3-chlorotetrahydrofuran, whereas Kerestzy and Wolf's material gives only a small yield of impure halogen-containing products.



Reformulation of Kerestzy and Wolf's product as 3 : 5-dichloropentan-2-one (III) is consistent with the patent claim that it yields vitamin B_1 when treated with 4-amino-2-methyl-5-thioformamidomethylpyrimidine.

Experimental.—3 : 5-*Dichloropentan*-2-*one*. Sulphuryl chloride (327 g.) was added dropwise to acetylbutyrolactone (308 g.) during 90 min. and the mixture kept for 12 hr. Water (100 ml.) was added and the product isolated with ether. Evaporation gave crude acetylchlorobutyrolactone (376 g.) which was treated with concentrated hydrochloric acid (188 ml.) and heated to 30—50° for 3 hr. with stirring. Hydrogen chloride was passed through the cooled mixture (ice) for 2½ hr. and the product extracted with light petroleum (b. p. 60—80°). The solvent was removed and the residue distilled, three fractions being taken : (1) b. p. 86—88°/15 mm. (101 g.), n_D^{23} 1·4621; (2) b. p. 88—105°/15 mm. (55 g.), n_D^{23} 1·4657; (3) b. p. 105—135°/15 mm. (42 g.), n_D^{23} 1·4800. Refractionation of (1) and (2) gave 3 : 5-*dichloropentan*-2-*one* (131 g.), b. p. 53°/0·4 mm., 99°/15 mm., n_D^{20} 1·4632 (Found : C, 39·3; H, 4·85; Cl, 45·25. $C_5H_8OCl_2$ requires C, 38·8; H, 5·2; Cl, 45·75%). A yellow 2 : 4-*dinitrophenylhydrazone* crystallised in plates or needles (from ethanol), m. p. 133—135° (Found : C, 39·75; H, 3·9. $C_{11}H_{12}O_4N_4Cl_2$ requires C, 39·4; H, 3·6%). Recrystallisations from 95% ethanol cause deterioration of the m. p. The ketone gave a violet colour with *m*-dinitrobenzene and sodium hydroxide and a positive Adachi test for a methyl ketone (*Analyt. Chem.*, 1951, **23**, 1491). It reduced Fehling's solution, and gave a silver mirror with ammoniacal silver nitrate. Schiff's test was negative. Paul and Tchelitcheff (*loc. cit.*) give b. p. 56—58°/20 mm., n_D^{20} 1·4804, for 2 : 3-dichlorotetrahydro-2-methylfuran. 1 : 4-Dichloropentan-3-one (Catch, Elliot, Hey, and Jones, *J.*, 1948, 278) has b. p. 64—65°/1·5 mm., n_D^{20} 1·4631.

When 3 : 5-dichloropentan-2-one was treated with methylmagnesium bromide and worked up in the usual way, a small yield of distillable material was formed. This was fractionated at 15 mm., five cuts being taken between 80° and 125°. Refractive indices ranged from n_D^{20} 1·4519 to 1·4758 and chlorine contents from 17·9 to 35·7%, but no homogeneous material was isolated.

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Reaction of 1-(*Nitrophenyl*)*pyrazoles with Alkali.*

By H. P. CROCKER and R. H. HALL.

[Reprint Order No. 6593.]

ATTEMPTED purification of a sample of 1-(2 : 4-dinitrophenyl)pyrazole by percolation of its benzene solution through a column of activated alumina gave a large zone of strongly adsorbed, bright yellow material, which could not be eluted with benzene. Similar results were obtained with a pure specimen; in this case, subsequent elution of the column with methanol rapidly removed a colourless basic substance and then, more slowly, the yellow material. The base was proved to be pyrazole by direct comparison with an authentic specimen and the yellow substance was identified as sodium 2 : 4-dinitrophenoxide by elementary analysis, comparison with an authentic specimen, and conversion into 2 : 4-dinitrophenol and 2-bromo-4 : 6-dinitrophenol.

The decomposition of the dinitrophenylpyrazole on the alumina was obviously due to the presence of traces of alkali in the latter, but the ease with which it occurred was remarkable. Several commercial samples of alumina behaved similarly, but a sample of acid-treated alumina was, as expected, much less effective. The dinitro-compound was stable to cold aqueous sodium hydroxide but it was rapidly cleaved by hot concentrated aqueous-methanolic sodium hydroxide and with boiling methanolic sodium methoxide a very clean conversion into pyrazole and 2 : 4-dinitroanisole was achieved.

The nucleophilic displacement of the pyrazole ring by a hydroxyl or methoxyl group in these reactions was clearly induced by the two powerful electron-attracting nitro-groups in the *ortho-para*-positions in the benzene ring (cf. Bunnett and Zahler, *Chem. Reviews*, 1951, **49**, 273; Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 797). The presence of only one such group, as in 1-*p*-nitrophenylpyrazole, provided insufficient activation for reaction to occur under similar conditions, the mononitro-compound being recovered unchanged from passage of its benzene solution through alumina or from a short treatment with boiling methanolic sodium methoxide.

Experimental.—Materials. 1-(2 : 4-Dinitrophenyl)pyrazole, pale lemon-coloured prisms, m. p. 109—109·5° (from methanol), and 1-*p*-nitrophenylpyrazole, m. p. 170°, were prepared essentially by Copenhaver's method (U.S.P. 2,515,160, 2,527,533). Finar and Godfrey (*J.*, 1954, 2293) were unable to obtain the dinitro-compound by this method.

Chromatography of 1-(2 : *4-dinitrophenyl)pyrazole.* A solution of pure 1-(2 : 4-dinitrophenyl)-pyrazole (687 mg.) in benzene (70 ml.) was added to a column (60 × 1·5 cm. diameter) of chromatographic alumina (Hopkin and Williams Ltd.), packed in benzene. A large bright yellow zone was obtained. Elution with benzene (500 ml.) gave only a trace (9 mg.) of gum which was not examined further. Elution with methanol (200 ml.) furnished an almost colourless solid (135 mg.) which sublimed at 60—70°/11 mm. to give colourless needles (129 mg., 65%) of pyrazole, m. p. 69—70°, undepressed on admixture with an authentic specimen (Dornow and Peterlein, *Chem. Ber.*, 1949, **82**, 257). Further elution of the column with methanol (800 ml.) afforded sodium 2 : 4-dinitrophenoxide monohydrate (588 mg., 89%), m. p. and mixed m. p. 307° (decomp.). The hydrated sodium salt separated from *n*-butyl alcohol as small yellow needles, m. p. 311—312° (decomp.) (Found : C, 32·7; H, 2·4; N, 12·1; Na, 9·7. Calc. for $C_6H_3O_5N_2Na,H_2O$: C, 32·15; H, 2·25; N, 12·5; Na, 10·25%). Continuous ether-extraction of a mixture of the crude sodium salt (320 mg.) with excess of dilute hydrochloric acid gave 2 : 4-dinitrophenol (256 mg.), m. p. 113°, which crystallised from aqueous ethanol as plates, m. p. and mixed m. p. 114°. The dinitrophenol was characterised as 2-bromo-4 : 6-dinitrophenol, m. p. and mixed m. p. 117°.

Two other commercial samples of activated alumina (Savory and Moore Ltd., " for chromatographic analysis," Grade II, and Peter Spence, Type A) gave similar results. A sample of Peter Spence, Type A, alumina which had been steeped in dilute sulphuric acid at pH 4 for several minutes, then washed with water and dried, was much less effective.

Treatment of 1-(2 : *4-dinitrophenyl)pyrazole with sodium hydroxide.* A mixture of the dinitrophenylpyrazole (500 mg.), methanol (10 ml.), and aqueous sodium hydroxide (5 ml., 40% w/v) was refluxed for 10 min. under nitrogen. The dark-brown solution was diluted with water (50 ml.) and extracted continuously with ether. The extract was concentrated and the small amount of aqueous-methanolic solution which remained was dehydrated azeotropically with methylene dichloride to give, after removal of solvent, a mixture of a yellow solid and colourless crystals. This was triturated with ether (2 × 50 ml.) and filtered, leaving a yellow solid as residue.

The filtrate was concentrated to give a slightly oily, yellowish-brown solid (130 mg.), a portion of which on sublimation at 60°/12 mm. furnished colourless crystals of pyrazole, m. p. and mixed m. p. 68—69°. A second portion (58 mg.) gave a picrate (150 mg.), m. p. 159—161°, raised to 160—161° on recrystallisation from benzene. Admixture with authentic pyrazole picrate (m. p. 162—163°) gave a mixed m. p. of 161—162°.

The yellow solid insoluble in ether was dissolved in methanol, the solution filtered, and the solvent removed to give sodium 2 : 4-dinitrophenoxide (334 mg.), from a portion (169 mg.) of which 2 : 4-dinitrophenol (122 mg.), m. p. and mixed m. p. 113—114°, was prepared by acidification of a concentrated aqueous solution. A further quantity (35 mg.) of dinitrophenol (slightly impure), m. p. 111° (mixed m. p. 112—113°), was obtained from the aqueous solution remaining after the continuous ether-extraction above by acidification followed by continuous ether-extraction.

Treatment of 1-(2 : *4-dinitrophenyl*)*pyrazole with sodium methoxide.* A mixture of the dinitro-compound (3·59 g.), methanol (60 ml.), and methanolic sodium methoxide (35 ml.; 0·606N) was refluxed under nitrogen for 5 min. The resulting dark-brown solution was poured into water (300 ml.) containing a slight excess of hydrochloric acid, and the pale-cream crude 2 : 4-dinitroanisole (2·95 g., 98%) which separated on cooling was collected. The m. p., 88°, was not changed by chromatography on alumina from benzene, followed by elution with carbon tetrachloride–benzene (1 : 1 by vol.) and subsequent recrystallisation from aqueous ethanol, or by admixture with an authentic specimen, m. p. 88° (recorded m. p.s range from 87° to 96°).

The acidic filtrate obtained as above was extracted with ether (3 × 50 ml.), basified with sodium hydroxide solution, and extracted continuously with ether. One-half of the dried (Na_2SO_4) extract was concentrated and the residue sublimed at 60°/12 mm.; it gave colourless crystals of pyrazole, m. p. and mixed m. p. 68—69°. To the other half was added a slight excess of picric acid, and the resulting solution was concentrated to give pyrazole picrate (1·32 g., 58%), m. p. 155—156°. One recrystallisation from ethanol raised the m. p. to 162—163°, undepressed on admixture with an authentic specimen.

The authors are indebted to Messrs. D. A. Burch and T. E. Couling for technical assistance.

THE DISTILLERS CO., LTD., RESEARCH AND DEVELOPMENT DEPT.,
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Some Reactions of o-*Nitrobenzenesulphenyl Bromide.*

By A. BURAWOY, P. RAYMAKERS, and C. TÜRNER.

[Reprint Order No. 6657.]

SULPHENYL halides are known to condense with phenolic substances such as 2-naphthol and with ketones such as acetone and acetophenone, and to add to olefinic double bonds to form sulphides. Most of the investigations have been carried out with the chlorides, the bromides often being assumed to react in a similar manner. Zincke and Röse (*Annalen*, 1914, **406**, 103), however, observed that 3-nitrotoluene-4-sulphenyl bromide, in contrast to its chloride, with acetone gives bromoacetone and 2 : 2′-dinitro-4 : 4′-ditolyl disulphide, and Kharasch and Bruice (*J. Amer. Chem. Soc.*, 1951, **73**, 3240) noted that fluorenone-1-sulphenyl bromide, unlike its chloride, is converted into the disulphide when heated with acetone, no reference to the fate of the bromine being made.

In the course of other work, we have found that *o*-nitrobenzenesulphenyl bromide reacts with 2-naphthol, acetophenone, or cholesteryl acetate in cold dry ether to yield the disulphide in addition to 1-bromo-2-naphthol, phenacyl bromide, and 5 : 6-dibromocholestanyl acetate respectively, whereas with *cyclo*hexene it behaves like the chloride (Kharasch, Wehrmeister, and Tigermann, *ibid.*, 1947, **69**, 1612), the addition product 2-bromo*cyclo*hexyl *o*-nitrophenyl sulphide being formed. An addition product with 1 : 4-dihydronaphthalene has been recently described by Kharasch, Buess, and Strachan (*ibid.*, 1952, **74**, 3422).

Bromination is probably initiated by slow dissociation of *o*-nitrobenzenesulphenyl bromide into the disulphide and bromine, the latter subsequently reacting in the normal way. This would be similar to the observation that the formation of thiocyanogen and the disulphide occasionally replaces the addition of a sulphenyl thiocyanate to an olefin (Kharasch, Wehrmeister, and Tigermann, *loc. cit.*).

The formation of new addition products of *p*-nitrobenzenesulphenyl chloride and of anthraquinone-1-sulphenyl bromide with *cyclo*hexene is also reported.

Experimental.—*Action of* o-*nitrobenzenesulphenyl bromide on* 2-*naphthol.* A solution of 2-naphthol (1·3 g.) and the sulphenyl bromide (4·7 g.) in dry ether (50 c.c.) was kept for 10 days at room temperature. Hydrogen bromide was evolved and almost pure 2 : 2′-dinitrodiphenyl disulphide separated [2·75 g.; m. p. and mixed m. p. 195° (from benzene)]. Steam-distillation of the mother-liquor yielded 1-bromo-2-naphthol [1·4 g., 70%; m. p. and mixed m. p. 83—84°, (from light petroleum)].

Action of o-*nitrobenzenesulphenyl bromide on acetophenone.* A solution of acetophenone (1·2 g.) and the sulphenyl bromide (4·7 g.) in dry ether (50 c.c.) was kept for 6 days at room temperature. Hydrogen bromide was evolved and almost pure 2 : 2′-dinitrodiphenyl disulphide separated [2·75 g.; m. p. 195° (from benzene)]. Steam-distillation of the mother-liquor yielded phenacyl bromide [1·0 g., 52%; m. p. and mixed m. p. 50° (from aqueous ethanol)].

Action of o-*nitrobenzenesulphenyl bromide on cholesteryl acetate.* A solution of cholesteryl acetate (4·3 g.) and the sulphenyl bromide (4·7 g.) in ether (50 c.c.) was kept for 30 days. 2 : 2′-Dinitrodiphenyl disulphide crystallised out [2·6 g.; m. p. 195° (from benzene)]. After removal of ether from the mother-liquor under reduced pressure, the residue crystallised from ethanol to give needles of 5 : 6-dibromocholestanyl acetate [1·6 g., 27%; m. p. 115—116°, not depressed by a specimen prepared by the action of bromine in carbon tetrachloride on cholesteryl acetate (Wislicenus and Moldenhauer, *Annalen*, 1868, **146**, 178)].

Action of o-*nitrobenzenesulphenyl bromide on* cyclo*hexene.* A solution of the sulphenyl bromide (5 g.) and *cyclo*hexene (5 g.) in dry ether (50 c.c.) was kept for 24 hr. 2-*Bromo*cyclo*hexyl* o-*nitrophenyl sulphide* separated (5·3 g., 79%). Crystallisation from ethanol gave large yellow prisms, m. p. 96·5—97·5° (Found: C, 45·7; H, 4·5. $C_{12}H_{14}O_2NSBr$ requires C, 45·6; H, 4·4%). No hydrogen bromide could be detected. A similar result was obtained in a reaction in boiling carbon tetrachloride.

Action of p-*nitrobenzenesulphenyl chloride on* cyclo*hexene.* A solution of the sulphenyl chloride (3·8 g.) and *cyclo*hexene (5 g.) in dry ether (50 c.c.) was kept for 3 days at room temperature. Ether and excess of *cyclo*hexene were removed under reduced pressure and the crystalline residue of 2-*chloro*cyclo*hexyl* p-*nitrophenyl sulphide* was washed with light petroleum and collected (4·6 g., 85%). Crystallisation from light petroleum (b. p. 40—60°) gave yellow prisms, m. p. 66—67° (Found: C, 53·4; H, 5·1. $C_{12}H_{14}O_2NSCl$ requires C, 53·0; H, 5·2%). No hydrogen bromide could be detected. A similar result was obtained in a reaction in boiling carbon tetrachloride.

Action of anthraquinone-1-*sulphenyl bromide on* cyclo*hexene.* The sulphenyl bromide (2·7 g.), *cyclo*hexene (2·1 g.), and dry carbon tetrachloride (50 c.c.) were refluxed for 30 hr. After removal of the solvent 1-*anthraquinonyl* 2-*bromo*cyclo*hexyl sulphide* was collected almost quantitatively (3·2 g.). Crystallisation from acetic acid gave light brown needles, m. p. 169—170° (Found: C, 59·6; H, 4·4. $C_{20}H_{17}O_2SBr$ requires C, 59·8; H, 4·2%).

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