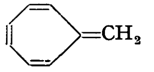
Some cyclo*Heptatriene Derivatives.*

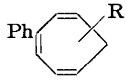
By J. H. P. van Aardt.

[Reprint Order No. 4103.]

Attempts to prepare heptafulvenes, such as (I), from *cyclo*heptatriene derivatives, failed. In one attempt the dehydration of a *cyclo*heptatriene alcohol (II; $R = CH_2 \cdot OH$) was investigated. With phosphoric oxide only polymers were formed. However, passage over alumina at 350° and fractional distillation and chromatography of the green product afforded 4-phenylstyrene, a straw-coloured liquid ($C_{14}H_{14}$), a green polymeric hydrocarbon and a dark blue azulene-like hydrocarbon.

(I)





(II)

Similar products, except for 4-phenylstyrene, were also formed when the alcohol was heated with a palladium–charcoal catalyst. The $C_{14}H_{14}$ hydrocarbon had an absorption spectrum identical with that of the alcohol from which it was derived, and it is therefore concluded that it is a methylphenyl*cyclo*heptatriene (II; $R = Me$), formed by disproportionation. The green viscous hydrocarbon had analytical figures corresponding to $C_{28}H_{24}$. The blue substance, in addition to its solubility in 85% phosphoric acid, was distinguished by an absorption spectrum similar to that of 1 : 2-benzazulene (Nunn and Rapson, *J.*, 1949, 825). It was formed in very small amount only.

Another unsuccessful approach was through ethyl benzyl*cyclo*heptatrienecarboxylate, which was brominated with *N*-bromosuccinimide. The product was dehydrobrominated with quinoline but no characterisable products were isolated.

In a third series of experiments, a methoxymethyl ester formed by esterification of the product of interaction of diazoacetic ester with diphenylmethyl acetate was treated with phosphoric oxide in benzene, yielding methyl stilbene-4-carboxylate as the only characterisable product.

It would appear that the heptafulvene system is not readily obtained by elimination reactions, as long as the seven-membered ring is unprotected against competing rearrangement reactions.

Experimental.—*Phenyl*cyclo*heptatrienecarboxylic acid.* Diazoacetic ester (10 g.) was added dropwise with constant stirring to diphenyl (100 g.) at 120—130°. When addition was complete the temperature was raised to 160° during 2 hr. A hot alcoholic solution of the mixture was cooled, whereupon most of the excess of diphenyl crystallised out and was filtered off. Alcoholic potash was added to the filtrate, and the acidic crystalline product (6 g.) was separated in the usual way and crystallised from aqueous alcohol, forming slightly yellow plates, m. p. 155·5° (Found: C, 79·2; H, 5·7. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%). Absorption spectrum: $\lambda_{max.}$ 236, 315 mμ; log ε 4·15, 3·98. On oxidation with aqueous potassium permanganate the acid yielded benzoic acid.

*Phenyl*cyclo*heptatrienylmethanol.* Ethyl phenyl*cyclo*heptatrienecarboxylate (10 g.) was added dropwise with vigorous stirring to a solution of lithium aluminium hydride (1 g.) in ether (30 c.c.). At the end of the addition the excess of hydride was decomposed with a little water, and the reaction mixture was poured into water, and 10% sulphuric acid added. The ethereal solution was washed with water, and the ether removed. The yellow oily residue was treated with sodium hydroxide in alcohol and water to remove unchanged ester, and the neutral fraction distilled in *vacuo*, yielding a slightly yellow oil (8 g.), b. p. 140°/0·25 mm. (Found: C, 84·7; H, 7·4%; H_2 absorbed in presence of Pd–$CaCO_3$ catalyst, 3·0 mol. Calc. for $C_{14}H_{14}O$: C, 84·8; H, 7·1%). Absorption spectrum: $\lambda_{max.}$ 299, 236 mμ; log ε 3·94, 4·19.

*Dehydration of phenyl*cyclo*heptatrienylmethanol.* (*a*) Over aluminia at 350°; (*b*) in presence of palladium–charcoal catalyst. These experiments yielded as main fraction a pale yellow liquid, b. p. *ca.* 92°/0·5 mm. (Found: C, 92·3; H, 7·7%; H_2 absorbed in presence of Pd–$CaCO_3$ catalyst, 3 mol. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%). The absorption spectrum of this substance was identical with that of the original carbinol.

*Ethyl benzyl*cyclo*heptatrienecarboxylate.* Diphenylmethane (100 g.) was treated with diazoacetic ester (10 g.) as described above for the reaction with diphenyl. The acidic product could not be crystallised and was therefore re-esterified and the ester purified by distillation. It distilled as a viscous yellow oil, b. p. 156°/1·5 mm. (Found: C, 80·0; H, 7·3%; sap. equiv., 254. Calc. for $C_{17}H_{18}O_2$: C, 80·3; H, 7·1%; sap. equiv., 254). Absorption spectrum: $\lambda_{max.}$ 285 mμ; log ε 3·65.

Microanalyses were by Mr. E. Schöning.

The author thanks Dr. W. S. Rapson, Dr. D. H. S. Horn, and Dr. D. A. Sutton for advice and assistance. This note is published with the permission of the South African Council for Scientific and Industrial Research.

NATIONAL CHEMICAL RESEARCH LABORATORY,
SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH,
PRETORIA, SOUTH AFRICA.
[*Received, December 29th,* 1952.]

Butadienes and Related Compounds. Part II. Factors affecting the Conversion of Asymmetric Di-*p*-substituted Phenylethylenes on Bromination into* 1 : 1 : 4 : 4-*Tetra-arylbuta-*1 : 3-*dienes.*

By WADIE TADROS.

[Reprint Order No. 5098.]

THE induction period (Tadros and Aziz, Part I *) which precedes formation of 1 : 1 : 4 : 4-tetra-*p*-alkoxyphenylbuta-1 : 3-diene from the ethylene and vinyl bromide in boiling acetic acid varied (see Table) with the amount of water present in the solvent. Now free-radical formation would be favoured by solvents of low dielectric constant (Waters, "The Chemistry of free Radicals," Clarendon Press, Oxford, 1946, p. 16): dilution of acetic acid by addition of water or absorption of atmospheric humidity increases the dielectric constant. When the crude product from the bromination of the ethylene in chloroform or carbon tetrachloride is crystallised from boiling acetic acid, the butadiene is obtained, but this is due solely to the acetic acid. Nevertheless when the bromination mixture or the mixture of the ethylene and vinyl bromide in carbon tetrachloride saturated with hydrogen bromide was left at room temperature for several days, the butadiene was slowly formed (the *p*-*iso*propoxy-compound was not dealkylated in such experiments at room temperature; cf. Tadros and Aziz, *loc. cit.*). The vinyl bromides, when kept in the dark in acetic acid at room temperature for 18 months, were recovered unchanged; but when exposed to direct sunlight in acetic acid or carbon tetrachloride, in presence or absence of hydrogen bromide, they were oxidised to the benzophenones; a small amount of the butadiene was formed (probably during the night) when acetic acid was the solvent. However, the butadienes were readily formed in acetic acid (Tadros and Akhnookh, unpublished work) in direct sunlight when oxygen was excluded (comment on this finding and related experiments is postponed).

Addition of pyridine to a solution of the ethylene and the vinyl bromide in glacial acetic acid prevented reaction. Whereas the replacement of the alkoxy-compound by the *p*-dimethylamino-ethylene gave the butadiene on bromination in chloroform or carbon tetrachloride, the *p*-chloro-compound did not, even in boiling acetic acid. 1 : 1 : 4 : 4-Tetra-*p*-chlorophenylbuta-1 : 3-diene (Brand *et al.*, *J. pr. Chem.*, 1930, **127**, 219, 240) was obtained (together with other products) only when the crude product was heated at 280—300°. The structures of the *p*-chloro-butadiene and of 1 : 1-di-*p*-methoxyphenyl-4 : 4-di-*p*-*iso*propoxyphenylbuta-1 : 3-diene, which could be readily obtained, were confirmed by ozonolysis. The effect of hydrogen bromide on the formation of the butadienes has been emphasised (see Table).

---

* Part I, *J.*, 1951, 2553.

1 : 1-Di-*p*-benzyloxyphenylethanol was obtained—in larger proportions in large-scale experiments—on decomposition of the product from methylmagnesium iodide and 4 : 4'-dibenzyloxybenzophenone with cold aqueous ammonium chloride solution.

Experimental.—1 : 1-*Di*-p-*methoxyphenyl*-4 : 4-*di*-p-iso*propoxyphenylbuta*-1 : 3-*diene*. A solution of 1 : 1-di-*p*-*iso*propoxyphenylethylene (0·592 g.) and di-*p*-methoxyphenylvinyl bromide (0·64 g., 1 mol.) in glacial acetic acid (10 c.c.) was boiled for 2 min. The *butadiene* (0·9 g.; sinters at 150°, m. p. 175°) separated on cooling and, crystallised from acetic acid, was pale greenish-yellow (m. p. 155°; 0·75 g.) (Found: C, 80·2; H, 7·3. $C_{36}H_{38}O_4$ requires C, 80·9; H, 7·1%). On dilution of the acetic acid mother-liquor and fractional crystallisation of the precipitate from little acetic acid, 1 : 1 : 4 : 4-tetra-*p*-methoxy-, m. p. 204—205°, and 1 : 1 : 4 : 4-tetra-*p*-*iso*propoxy-phenylbuta-1 : 3-diene, m. p. 187°, showing no depression on admixture with authentic samples, were obtained. The possibility that the product of m. p. 155° was a mixture of these two butadienes was eliminated as follows: m. p.s of a mixture of the tetramethoxy- and the tetra*iso*propoxy-diene softened at 180° and melted at 195°; one of the tetramethoxy-diene and the diene of m. p. 155° softened at 155° and melted at 190°; one of the tetra*iso*propoxy-diene and the diene of m. p. 155° softened at 155° and melted at 165°.

1 : 1 : 4 : 4-*Tetra*-p-*chlorophenylbuta*-1 : 3-*diene*. A solution of bromine (6·4 g.) in carbon tetrachloride (10 c.c.) was added to one of 1 : 1-di-*p*-chlorophenylethylene (10 g.) (Grummit, Buck, and Becker, *J. Amer. Chem. Soc.*, 1945, **67**, 2265) in the same solvent (50 c.c.). The solvent was removed and the residue was heated at 280—300° for 15 min. The dark brown material thus obtained was triturated with acetone, a brown residue (m. p. above 320°) being undissolved. The acetone solution was filtered and solvent removed. The residue of *diene* crystallised from ethyl acetate as brownish-yellow crystals, m. p. 244° (1 g.) (Found: C, 67·3; H, 4·1; Cl, 28·2. Calc. for $C_{28}H_{18}Cl_4$: C, 67·7; H, 3·6; Cl, 28·6%).

Experiment	Solvent	Temp.	Induction period	R in *p*-subst. OR	Butadiene G.
I	99% AcOH	B. p.	2 min.	Me	0·75
	90% AcOH	B. p.	5–6 min.	Me	0·80
	80% AcOH	B. p.	15–20 min.	Me	0·25 (after 0·5 hr.)
	80% AcOH *	B. p.	1 min.	Me	0·25 (after 20 min.)
			Reaction period		
	CCl_4	B. p.	6 hr.	Me	0
	CCl_4 *	B. p.	6 hr.	Me	0·1
	99% AcOH or CCl_4	20—25°	25 days	Me or Et	0
	99% AcOH *	,,	,,	Me	0·85
				Et	0·95
	CCl_4 *	,,	,,	Me or Et	0·3
II	99% AcOH	,,	18 months	Me or Et	0
	99% AcOH *	,,	25 days	Me or Et	0·06
III	99% AcOH	,,	,,	Me, Et, or Pr^i	*ca.* 0·85
	CCl_4	,,	,,	Me or Et	0·3
				Pr^i	0·08
	CCl_4 †	B. p.	2 hr.	Me or Et	0

* Solvents saturated with HBr.

I. 1 : 1-Di-*p*-methoxy- (0·48 g., 1 mol.) or -ethoxy-phenylethylene (0·536 g., 1 mol.) and the corresponding vinyl bromide (methoxy-, 0·64 g.; ethoxy-, 0·694 g., 1 mol.), solvent (10 c.c.). With 80% AcOH, the mother-liquor was yellow, otherwise it was dark olive-green.

II. A solution of the di-*p*-alkoxyphenylvinyl bromide (0·5 g.) in the solvent (10 c.c.) was left in the dark. The solutions saturated with hydrogen bromide became rose within 24 hr., gradually changing to wine-red and then brown.

III. A solution of bromine (0·3 g.) in the solvent (2 c.c.) was added to one of the ethylene in the same solvent (8 c.c.). In these experiments the *iso*propoxy-compound did not undergo cleavage.

† A mixture of the ethylene and the corresponding vinyl bromide only (methoxy-, m. p. 84°; ethoxy-, m.p. 64°) was obtained.

The butadienes had m. p. and mixed m. p.: R = Me, 204—205°; Et, 207°; Pr^i, 187°.

1 : 1 : 4 : 4-*Tetra*-p-*dimethylaminophenylbuta*-1 : 3-*diene*. A solution of bromine (0·9 g.) in chloroform or carbon tetrachloride (2 c.c.) was added to one of 1 : 1-bis-*p*-dimethylaminophenylethylene (1·5 g.) (Freund and Mayer, *Ber.*, 1906, **39**, 1117) in the same solvent (12 c.c.). The solvent was removed, the residue was treated with a few c.c. of 3% aqueous sodium hydroxide, filtered off, washed with water, and treated with boiling alcohol, and the undissolved *butadiene* crystallised from acetone as brownish- or greenish-yellow crystals which softened at 274° and

melted at 282° (0·2 g.) (Found : C, 81·2; H, 7·7; N, 10·9. $C_{36}H_{42}N_4$ requires C, 81·5; H, 7·9; N, 10·6%).

1 : 1-*Di*-p-*benzyloxyphenylethanol.* 4 : 4′-Di-*p*-benzyloxybenzophenone (100 g.) was added to methylmagnesium iodide (from magnesium, 9·1 g., and methyl iodide, 54 g.) in ether (500 c.c.) with stirring, during 2 hr., and then left overnight. The mixture was decomposed with cold aqueous ammonium chloride and extracted with ether or benzene–ether. The *alcohol* crystallised from ethanol as colourless crystals, m. p. 87° (70 g.) (Found : C, 82·5; H, 6·0. $C_{28}H_{26}O_3$ requires C, 82·0; H, 6·3%).

Effect of sunlight on the alkoxy-vinyl bromides. On exposure to direct sunlight of a solution of di-*p*-methoxy(or -ethoxy)phenylvinyl bromide (0·5 g.) in acetic or carbon tetrachloride (10 c.c.) in a silica flask, the vinyl compound was oxidised to 4 : 4′-dimethoxy- (m. p. and mixed m. p. 142°) and 4 : 4′-diethoxy-benzophenone (m. p. and mixed m. p. 127°). The solution became successively yellow, wine-red, brown-red, and finally yellow (within 4—6 weeks depending on season of exposure) when the reaction was almost complete.

Ozonolysis. The butadienes (see Tadros and Aziz, *loc. cit.*) gave glyoxal, identified as its bis-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 318°, and the corresponding ketone. The *p*-chloro-butadiene gave 4 : 4′-dichlorobenzophenone, m. p. and mixed m. p. 144°. 1 : 1-Di-*p*-methoxyphenyl-4 : 4-di-*p*-*iso*propoxyphenylbuta-1 : 3-diene gave 4 : 4′-dimethoxy-, m. p. and mixed m. p. 142°, and 4 : 4′-di*iso*propoxybenzophenone, m. p. and mixed m. p. 72°, separated by fractional crystallisation from dilute alcohol.

CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE,
CAIRO UNIVERSITY, EGYPT.

[*Received, February 8th,* 1954.]

Tetrazolium Compounds. Part IV. C-Heterocyclic Derivatives.*

By (MISS) H. J. COTTRELL, D. L. PAIN, and R. SLACK.

[Reprint Order No. 5199.]

IN Parts II and III * of this series, formazans and tetrazolium salts bearing phenylazophenyl and styrylphenyl substituents were described. The present note deals with similar compounds in which a heterocyclic ring is attached to the carbon atom of the formazan chain or tetrazole nucleus.

The pyridine derivatives were prepared mainly to assess their potentialities as antitubercular agents since the 3-pyridylformazans and 5-pyridyltetrazolium salts have structural features in common with pyridine-4-carboxyhydrazide (" Isoniazid ").

Experimental.—The formazans (see Table 1) were prepared by the methods indicated in Part I (*J.*, 1953, 3881). Those carrying quaternary pyridine substituents were obtained by direct quaternisation of the simple pyridylformazans with methyl chloride, iodide, or sulphate in methanol.

Oxidations were effected with yellow mercuric oxide in methanol, and tetrazolium compounds (Table 2) were usually isolated as halides. The tetrazolium chloride from 1 : 5-diphenyl-3-4′-pyridylformazan was not obtained pure and was converted into the di(hydrogen sulphate) by treatment with methanolic sulphuric acid. 3-2′-Furyl-1 : 5-diphenylformazan is new but the corresponding tetrazolium chloride has been mentioned (Mattson, Jensen, and Dutcher, *Science*, 1947, **106**, 294; Bielig and Querner, *Z. Naturforsch.*, 1949, **4b**, 21) without details. This formazan was purified by chromatography on alumina.

4-Formyl-2-phenyl-2 : 1 : 3-triazole (Hann and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 735) gave the *phenylhydrazone*, pale yellow needles (from ethanol), m. p. 117° (Found : C, 68·4; H, 5·0; N, 26·6. $C_{15}H_{13}N_5$ requires C, 68·5; H, 5·0; N, 26·6%).

* Parts II and III, *J.*, 1954, 1565, 1568.

TABLE 1. *Formazans,* $\mathrm{Ph{\cdot}NH{\cdot}N{:}CR'{\cdot}N{:}N{\cdot}C_6H_4R}$-*p*.

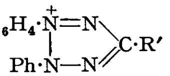
No.	R	R′	Yield (%)	M. p.	Appearance	Solvent
1	H	4-Pyridyl	46	185—187°	Red plates, golden reflex	$MeNO_2$
2	OMe	,,	95	158	Red needles, blue reflex	*cyclo*Hexane
3	Cl	,,	40	170—172	Red plates, golden reflex	$MeNO_2$
4	N:NPh	,,	39	194	Red needles, green reflex	Dioxan–H_2O
5	CH:CHPh	,,	40	184—187	,, ,,	,,
6*a*	H	4-*N*-Methylpyridinium chloride	80	210—212	,, ,,	H_2O
6*b*	H	4-*N*-Methylpyridinium iodide	92	233—234 †	,, ,,	$MeNO_2$
6*c*	H	4-*N*-Methylpyridinium methyl sulphate	81	204—205	Red needles, blue reflex	EtOH
7	CH:CHPh	4-*N*-Methylpyridinium iodide	84	200 †	,, ,,	$MeNO_2$
8	H	2-Furyl	14	118	Purple prisms. golden reflex	Light petroleum (b. p. 80—100°)
9	H	2-Phenyl-2 : 1 : 3-triazol-4-yl	59	163—164	Red needles, golden reflex	$MeNO_2$

† With decomp.

No.	Formula	Found (%) C	H	N	Hal.	Required (%) C	H	N	Hal.
1	$C_{18}H_{15}N_5$	71·3	5·25	23·5	—	71·8	5·0	23·3	—
2	$C_{19}H_{17}ON_5$	69·5	5·05	21·2	—	68·9	5·2	21·1	—
3	$C_{18}H_{14}N_5Cl$	—	—	21·0	10·8	—	—	20·9	10·6
4	$C_{24}H_{19}N_7$	—	—	23·7	—	—	—	24·2	—
5	$C_{26}H_{21}N_5$	—	—	17·2	—	—	—	17·4	—
6*a*	$C_{19}H_{18}N_5Cl$	—	—	19·2	10·0	—	—	19·9	10·1
6*b*	$C_{19}H_{18}N_5I$	—	—	16·7	29·1	—	—	15·8	28·7
6*c*	$C_{20}H_{21}O_4N_5S$ ‡	—	—	16·55	—	—	—	16·4	—
7	$C_{27}H_{24}N_5I$	—	—	12·6	23·2	—	—	12·8	23·3
8	$C_{17}H_{14}ON_4$	70·6	4·95	19·35	—	70·3	4·9	19·3	—
9	$C_{21}H_{17}N_7$	68·9	4·9	26·9	—	68·7	4·7	26·7	—

‡ Found : S, 7·8. Reqd. : S, 7·5%.

TABLE 2. *Tetrazolium salts,* *p*-$\mathrm{R{\cdot}C_6H_4{\cdot}}$



$$p\text{-}\mathrm{R{\cdot}C_6H_4{\cdot}\overset{+}{N}{=}N{\diagdown}C{\cdot}R'{\diagup}\!\!{=}N{-}N{\cdot}Ph}$$

No.*	Anion	Yield (%)	M. p.	Appearance	Solvent	Formula	Found (%) N	Hal	Reqd. (%) N	Hal
1	I [a]	47	226—227° †	Orange needles	EtOH	$C_{18}H_{14}N_5I$	16·2	30·1	16·4	29·8
2	Cl	58	157—160	Yellow needles	Pr^iOH	$C_{19}H_{16}ON_5Cl,HCl,2H_2O$	16·05	16·0	16·0	16·2
4	Br	32	178—180 (sinters at 158)	Scarlet prisms	H_2O	$C_{24}H_{18}N_7Br,H_2O$	19·7	15·9	19·5	15·9
5	Cl	51	213—216 †	Yellow prisms	,,	$C_{26}H_{20}N_5Cl,H_2O$	15·6	7·9	15·4	7·8
6	HSO_4 [b]	5	158—160	Pale yellow prisms	Dry EtOH	$C_{19}H_{19}O_8N_5S_2$ ‡	14·1	—	13·8	—
8	Cl	51	239—240	Pale yellow prisms	EtOH–Et_2O	$C_{17}H_{13}ON_4Cl$	17·1	11·0	17·2	10·9
9	Cl	40	253—254 †	Colourless needles	,,	$C_{21}H_{16}N_7Cl$	24·3	9·0	24·4	8·8

[a] The bromide has been described by Kuhn and Münzing (*Chem. Ber.*, 1953, **86**, 858). [b] The anion on the *N*-methylpyridinium moiety is also HSO_4.

* The tetrazolium salts have the R and R′ of the formazans of corresponding number in Table 1.

† With decomp. ‡ Found : S, 12·3. Reqd. : S, 12·6%.

The authors thank Mr. S. Bance, B.Sc., for semi-microanalyses and the Directors of May & Baker Ltd. for permission to publish these results.

RESEARCH LABORATORIES, MAY & BAKER LTD.,
DAGENHAM, ESSEX.

[*Received, March 11th,* 1954.]

The Infra-red Spectrum of Dideuteroglyoxal.

By J. C. D. Brand and G. J. Minkoff.

[Reprint Order No. 5217.]

Electron-diffraction experiments (LuValle and Shomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 3520) and the fine structure of certain infra-red bands (Cole and Thompson, *Proc. Roy. Soc.*, 1949, *A*, **200**, 10) have been interpreted in favour of the centrosymmetrical planar form of glyoxal (point-group, C_{2h}) as the configuration of lowest energy. The representation of the fundamentals is therefore $\Gamma = 5A_g + 2A_u + B_g + 4B_u$, six fundamentals being active in the infra-red and six in the Raman spectrum with mutual exclusion on account of the centre of symmetry. Cole and Thompson have assigned unequivocally four of the infra-red active fundamentals of normal glyoxal, and the remaining two almost certainly lie in the unmapped region beyond 15 μ. Because of experimental difficulties the Raman spectrum has not been measured, but the majority of the Raman-active fundamentals can be found in the ultra-violet spectrum (Thompson, *Trans. Faraday Soc.*, 1940, **36**, 988; Gaydon, *ibid.*, 1947, **43**, 36; Brand, *ibid.*, 1954, **50**, 431) and frequencies are listed in the Table for both normal and isotopic glyoxal where the assignment is believed to be certain or very probable.

Fundamental vibrational frequencies of glyoxal and dideuteroglyoxal.

				$C_2H_2O_2$	$C_2D_2O_2$	$\pi(\nu^i/\nu)^2$
A_g	R	CH, stretching	ν_1	2809	—	—
		CO, stretching	ν_2	1742	1722	—
		CHO, deformation	ν_3	—	—	—
		CC, stretching	ν_4	1201	—	—
		CHO, rocking	ν_5	553	537	—
A_u	IR	CH, wagging	ν_6	801·5 *	~630	—
		Torsional	ν_7	127	117	0·53 (calc., 0·52)
B_g	R	CH, wagging	ν_8	1048	911	0·76 (calc., 0·76)
B_u	IR	CH, stretching	ν_9	2836·2 *	2141	—
		CO, stretching	ν_{10}	1739	1712	—
		CHO, deformation	ν_{11}	1311·5 *	1008	—
		CHO, rocking	ν_{12}	—	—	—

Values marked * are from high-dispersion measurements by Cole and Thompson (*loc. cit.*). The A_g and B_g fundamental frequencies and the torsional frequency are taken from the ultra-violet spectrum. All measurements refer to the vapour.

Between 3 and 25 μ dideuteroglyoxal has only three regions of strong absorption (at 2141, 1712, and 1008 cm.$^{-1}$) which are clearly the B_u fundamentals ν_9, ν_{10}, and ν_{11}. At 1008 cm.$^{-1}$ the profile is of a type B band with maxima 8 cm.$^{-1}$ on either side of a central gap (cf. 10 cm.$^{-1}$ for normal glyoxal); the fact that the band is of type B is curious and the vibration must be a CHO planar deformation rather than a simple C–H rocking mode (type A). Of the remaining three infra-red-active fundamentals, the torsional mode certainly lies outside the region examined and the frequency in the Table is taken from the ultra-violet spectrum. The fundamental $\nu_6(A_u)$ was not visible with the available path of 0·3 cm.-at. of dideuteroglyoxal, and the frequency of ~630 cm.$^{-1}$ was calculated from the product rule. The missing B_u fundamental, ν_{12}, is quite uncertain: no absorption was found in the region 15—25 μ with a moderately long path (1 cm.-at.) of normal glyoxal but this might be due to low intensity and does not prove that the frequency lies below 400 cm.$^{-1}$; however it is noteworthy that the corresponding fundamental of buta-1 : 3-diene has been assigned provisionally at 320 cm.$^{-1}$ (Richards and Nielsen, *J. Opt. Soc. Amer.*, 1950, **40**, 438).

The assignment of the fundamentals in the present paper differs materially from that given by Thompson and by Gaydon (*locc. cit.*). The moments of inertia required for the product rule ratios, calculated from the electron-diffraction parameters, are:

$$\left.\begin{array}{ll} \text{for} & C_2H_2O_2: I_a = 8{\cdot}52,\ I_b = 103{\cdot}7 \text{ a.w.-Å}^2 \\ \text{for} & C_2D_2O_2: I_a = 12{\cdot}83,\ I_b = 104{\cdot}4 \end{array}\right\} \text{and } I_c = I_a + I_b$$

With the possible exception of the carbonyl frequencies it is clear that the A_g and B_g fundamentals do not appear in the infra-red, and the vibrational evidence for a centre of symmetry can be regarded as definite. Evidence for a plane of symmetry in addition to a centre, and hence for the species classification used in this paper, rests mainly on the electron-diffraction measurement. The spectroscopic evidence on this point is inconclusive, for the I_a's of the planar model and of the alternative (but structurally less plausible) centrosymmetrical non-planar configuration (S_2) are very similar and the fine structure of the infra-red bands is insensitive to deformation of the molecular plane.

Experimental.—Infra-red spectra were recorded with a double-beam spectrometer (Minkoff, *Fuel*, 1950, **3**, 221) with sodium chloride and potassium bromide optics. Dideuteroglyoxal was synthesised by mercury-photosensitised combination of deuterium and carbon monoxide.

THE UNIVERSITY, GLASGOW, W.2.
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.

[*Received, March* 19*th*, 1954.]

The Kinetics of Oxidation of Benzaldehyde. Part III. Note on the Reaction Catalysed by Benzoyl Peroxide.*

By M. F. R. MULCAHY and I. C. WATT.

[Reprint Order No. 5220.]

THE formation of hydroperoxide from liquid olefins and oxygen has been shown by Bolland and Gee and their collaborators (Bolland, *Quart. Reviews*, 1949, **3**, 1) to occur by the following mechanism :

$$\begin{array}{lllr}
\text{Initiation} & \longrightarrow & R\text{-} \text{ or } RO_2\text{-} \quad \ldots & (1)\\
R\text{-} + O_2 & \longrightarrow & RO_2\text{-} \quad \ldots\ldots & (2)\\
RO_2\text{-} + RH & \longrightarrow & ROOH + R\text{-} \quad \ldots & (3)
\end{array}
\qquad
\left.\begin{array}{ll}
R\text{-} + R\text{-} & \longrightarrow\\
R\text{-} + RO_2\text{-} & \longrightarrow\\
RO_2\text{-} + RO_2\text{-} & \longrightarrow
\end{array}\right\}\text{Termination}\left\{\begin{array}{r}. \ (4)\\ . \ (5)\\ . \ (6)\end{array}\right.$$

At sufficiently high oxygen concentration termination occurs by reaction (6) and the rate is given by :

$$\rho \equiv -d[O_2]/dt = k_3\,(R_i/k_6)^{\frac{1}{2}}[RH] \quad \ldots\ldots \quad (A)$$

where R_i is the rate of initiation. The kinetics of the oxidation of aldehydes differ in some respects from those of olefins, but Bowen and Tietz (*J.*, 1930, 234), Cooper and Melville (*J.*, 1951, 1984, 1994), Fillet, Niclause, and Letort (*Compt. rend.*, 1953, **236**, 1489), and Ingles and Melville (*Proc. Roy. Soc.*, *A*, 1953, **218**, 175) have shown that the kinetics of the photochemically initiated reaction conform to the requirements of equation (*A*). The experiments reported here were carried out to test the validity of equation (*A*) for the oxidation of benzaldehyde catalysed by benzoyl peroxide. The equation requires that at "high" oxygen concentrations the rate should be (*a*) proportional to $[Bz_2O_2]^{\frac{1}{2}}$, (*b*) proportional to [Ph·CHO], and (*c*) independent of $[O_2]$. Previous work (Part I) has shown that requirement (*a*) is fulfilled. However, the present experiments have been extended over a somewhat greater temperature range. The reaction was carried out in benzene solution, apparatus, experimental procedure, and methods of purification of reagents being as described in Part I.

Results.—(*a*) Fig. 1 shows the dependence of ρ on $[Bz_2O_2]^{\frac{1}{2}}$ at 4 temperatures. Each curve is linear over the whole range of peroxide concentration. As pointed out in Part I * this indicates that termination of the catalysed reaction occurs by mutual interaction of the chain-carriers, and that the rates of the catalysed reaction, ρ_c, and of the residual uncatalysed reaction, ρ_u, are

---

* Parts I and II, *Proc. Roy. Soc.*, 1953, *A*, **216**, 10, 30.

additive. Thus, the total rate of oxidation in the presence of added peroxide is given by $\rho_t = \rho_c + \rho_u$, where $\rho_c \propto [Bz_2O_2]^{\frac{1}{2}}$. The activation energy for ρ_c may be derived from an Arrhenius plot of the slopes (obtained by the method of least squares) of the lines in Fig. 1 (see Fig. 2, curve *A*). Thus E_c = 17·2 kcal./mole. Fig. 2 also shows (curve *B*) a plot of $\log_{10} \rho_u$ against $1/T$; this gives 13·6 kcal. for the apparent activation energy of the thermal reaction under these conditions.

(*b*) Values of ρ_c obtained at several concentrations of benzaldehyde with constant oxygen pressure and $[Bz_2O_2]$ are given in Table 1. ρ_c (penultimate column) was obtained by subtracting ρ_u from ρ_t and correcting the result (${}^1\rho_c$) for the small variations in $[Bz_2O_2]$ which resulted from the method of preparation of the solution. The constancy of ρ_c/[Ph·CHO] (last column) within the experimental error shows that the dependence of ρ_c on [Ph·CHO] is linear over the range of [Ph·CHO] allowed by the experimental conditions.

FIG. 1. *Variation of rate of oxygen absorption with square root of benzoyl peroxide concentration. Oxygen pressure* = 523 *mm.; benzaldehyde* = 0·224 *mole fraction in benzene.*

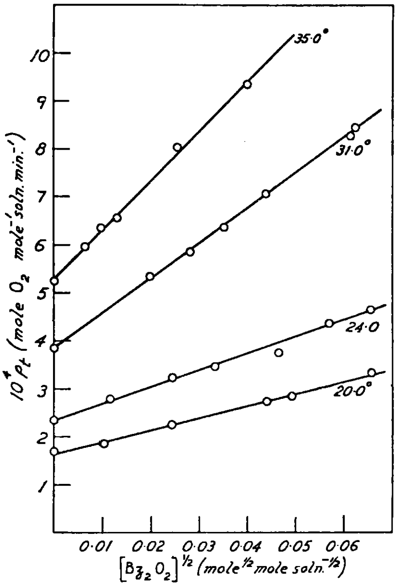


FIG. 2. *Dependence on temperature of* (*A*) *slope of* ρ_c–$[Bz_2O_2]^{\frac{1}{2}}$ *relationship and of* (*B*) ρ_u.

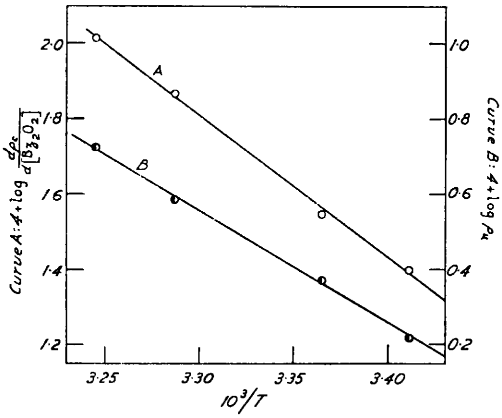


TABLE 1. *Values of* ρ_t, ρ_u, *and* ρ_c *at various benzaldehyde concentrations.*

Oxygen pressure = 523 mm.; $[Bz_2O_2]$ = 2·95 × 10^{-3} mole/mole soln.; *T* = 31·0°.†

Ph·CHO, mole fraction	ρ_t	ρ_u	${}^1\rho_c = \rho_t - \rho_u$	ρ_c	$10^3\rho_c$/[Ph·CHO]
		10^4 (mole O_2/mole soln. min.) †			
0·0446	0·88	0·05	0·83	0·84	1·88
0·0878	2·30	0·61	1·69	1·69	1·92
0·133	3·83	1·24	2·59	2·59	1·95
0·179	5·96	2·62	3·34	3·33	1·86
0·224	7·79	3·80	3·99	3·96	1·77

† In these units soln. means benzaldehyde + benzene.

(*c*) Values of ρ_c obtained at different oxygen pressures and constant concentrations of aldehyde and peroxide are given in Table 2 (last column).

The results show that over the range of oxygen concentration corresponding to the pressure range indicated, ρ_c is substantially independent of $[O_2]$.

TABLE 2. *Values of* ρ_t, ρ_u, *and* ρ_c *at various oxygen pressures.*

	ρ_t	ρ_u *	$\rho_c = \rho_t - \rho_u$
P_{O_2}, mm.	10^4 (mole O_2/mole soln. min.) †		
(i) Mole fraction Ph·CHO = 0·133; $[Bz_2O_2] = 2{\cdot}95 \times 10^{-3}$ mole/mole soln.; $T = 31{\cdot}0°$.†			
579	3·87	1·21	2·66
522	3·83	1·24	2·59
417	3·65	1·30	2·35
338	3·78	1·33	2·45
(ii) Mole fraction Ph·CHO = 0·045; $[Bz_2O_2] = 11{\cdot}08 \times 10^{-3}$ mole/mole soln.; $T = 31{\cdot}0°$.†			
497	2·26	0·05	2·21
271	2·46	0·07	2·39
105	2·37	0·13	2·24

* Interpolated values (Mulcahy and Watt, *loc. cit.*).

† In these units soln. means benzaldehyde + benzene.

Discussion.—The results are in agreement with expectation based on the mechanism proposed by Bolland and Gee, which therefore may be considered to apply to the peroxide-catalysed oxidation (at high concentrations of oxygen). From equation (*A*) it follows that $E_c = \frac{1}{2}E_i + E_3 - \frac{1}{2}E_6 = 17{\cdot}2$ kcal.*

E_i may be equated to the dissociation energy of the O–O bond in benzoyl peroxide. Setting $E_i = 29{\cdot}8$ kcal./mole (Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426; Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216) and $\frac{1}{2}E_6 \simeq 0$ (Bolland, *Trans. Faraday Soc.*, 1950, **46**, 358; Ingles and Melville, *loc. cit.*), we obtain $E_3 = 2{\cdot}3$ kcal. This agrees within experimental error with the value $E_3 = 1{\cdot}8$ kcal. derived from the photoinitiated reaction (in *n*-decane solution) by Ingles and Melville. It is noteworthy that the value of E_3 for benzaldehyde is smaller than the corresponding value obtained with any of the fifteen olefinic compounds studied by Bolland (*loc. cit.*).

By setting R_i equal to twice the rate of dissociation of benzoyl peroxide (R_{O-O}) into radicals (Bateman and Morris, *Trans. Faraday Soc.*, 1952, **48**, 1149) the magnitude of $k_3k_6^{-\frac{1}{2}}$ may be derived from the present results and those of Bawn and Mellish (*loc. cit.*) for R_{O-O} (in benzene solution). The value at 25° is given in Table 3 together with values calculated from the results of Melville *et al.* for benzaldehyde and *n*-decanaldehyde and that obtained by Bateman and Morris (*Trans. Faraday Soc.*, 1953, **49**, 1026) for 2 : 6-dimethylhepta-2 : 5-diene. Two points emerge from the Table : our value for $k_3k_6^{-\frac{1}{2}}$ does not agree with that of Melville and his collaborators for benzaldehyde (it is closer to their result for *n*-decanaldehyde) and it is about seven times greater than the corresponding value for dimethylheptadiene (cf. Bateman and Morris, *loc. cit.*). This difference between benzaldehyde and the olefins is thus in the same sense as the difference in the values of E_3. For equal rates of initiation and [RH], the chain length, ν, is proportional to $k_3k_6^{-\frac{1}{2}}$ and is therefore greater with benzaldehyde than with the olefins. Under the conditions of our experiments ν is of the order of 10^4—10^5.

TABLE 3.

	Initiator	$k_3k_6^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$	Solvent	Author
Benzaldehyde	benzoyl peroxide	0·85	benzene	Present work
Benzaldehyde	photochemical	0·16	*n*-decane	Ingles and Melville
n-Decanaldehyde	photochemical	0·7	*n*-decane	Cooper and Melville
2 : 6-Dimethylhepta-2 : 5-diene	AZDN	0·13	pure liquid	Bateman and Morris

Note on the Uncatalysed Reaction.—The value $E_u = 13{\cdot}6$ kcal. for the uncatalysed reaction with Ph·CHO mole fraction = 0·224 (Fig. 2) falls between the values 17·5 and 6 kcal. obtained (Part II) for " low " and " high " concentrations of benzaldehyde, respectively. Ingles and Melville using a solution of benzaldehyde of 0·32 mole fraction in *n*-decane find

---

* It is to be observed that the value of E_c is close to that of E_u at " high " oxygen concentrations (17·5 kcal.; cf. Part II) though the significance of the coincidence (if any) is not clear at present.

a value of 7·6 kcal. The reason for the discrepancy is at present obscure. We have found (unpublished) $E_{\text{u}} = 7{\cdot}7$ kcal. for pure undiluted benzaldehyde oxidizing under 617 mm. of oxygen.

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION,
DIVISION OF TRIBOPHYSICS, UNIVERSITY OF MELBOURNE, CARLTON, N.3,
VICTORIA, AUSTRALIA.

[*Received, March* 19*th*, 1954.]

*Reactions of Aromatic Nitro-compounds with Alkaline Sulphides. Part V.** 2 : 3-, 2 : 6-, *and* 1 : 7-*Dinitronaphthalenes.*

By E. R. WARD, T. M. COULSON, and J. G. HAWKINS.

[Reprint Order No. 5252.]

THE reduction with almost neutral aqueous methanolic sodium hydrogen sulphide of dinitronaphthalenes (cf. Part III, Hodgson and Ward, *J.*, 1949, 1187) has now been extended to the 2 : 3-, 2 : 6-, and 1 : 7-isomers. In each case the initial products were a nitronaphthylamine and the corresponding sodium nitronaphthyl sulphide. The yield of 3-nitro-2-naphthylamine is a considerable improvement on that obtained by van Rij, Verkade, and Wepster (*Rec. Trav. chim.*, 1951, **70**, 236) who used sodium disulphide, again emphasising the advantage of our method of selective reduction.

The percentage conversions of starting material into (*A*) nitronaphthylamine and (*B*) sodium nitronaphthyl sulphide, for the 10 dinitronaphthalenes are (cf. Part III) :

Isomer	1 : 2	1 : 3	1 : 4	2 : 3	1 : 5	1 : 6	1 : 7	1 : 8	2 : 6	2 : 7
A	0	82 *	5	69	55—58	60—62	38	0	70	80
B	100	18	95	31	45—42	40—38	62	100	30	20

* In this case a mixture of isomeric nitronaphthylamines.

Whilst we agree with Hodgson and Ward (*loc. cit.*) that the important factor is the electropositivity of the carbon atom to which the attacked nitro-group is attached, we cannot satisfactorily interpret the reactions on the basis of a quinonoid hypothesis (Vesely and Jakes, *Bull. Soc. chim.*, 1923, **33**, 955; Hodgson and Hathway, *J. Soc. Dyers and Col.*, 1945, **61**, 283). Such an hypothesis suggests that transmission of electronic effects from one nucleus to the other in naphthalene derivatives is a general phenomenon. Internuclear activation has certainly been demonstrated for both electrophilic and nucleophilic reactions but is weak compared with effects transmitted within one nucleus (cf. Bunnett and Zahler, *Chem. Reviews*, 1951, **49**, 273).

Our present results show the abnormal behaviour of 1 : 3- and 1 : 8-dinitronaphthalene, which is accentuated by detailed comparison with the reactivity of 1 : 5-dinitronaphthalene and 1 : 3 : 8-trinitronaphthalene (Hodgson and Ward, *J.*, 1945, 794; 1947, 1109) with aqueous methanolic sodium hydrogen sulphide. 1 : 3- and 1 : 8-Dinitronaphthalenes show other unusual properties (Ward, Thesis, London Univ., 1946). We consider that surveys of the reactivity of complete groups of naphthalene derivatives are necessary before satisfactory general interpretation of the reactivity of naphthalene compounds can be made.

Experimental.—The procedures followed for reduction and for isolation of products are described in Part III. Preliminary runs indicated the approximate proportions of products, and the amount of reducing agent required for complete conversion. As a further precaution reducing agent was added until a " permanent excess " was detectable in the reaction mixture. In each case the amount of reducing agent required was in reasonable agreement with that calculated from the yield of nitronaphthylamine, it being assumed that the other product was the sodium nitronaphthyl sulphide.

1 : 7-*Dinitronaphthalene.* The 8-nitro-2-naphthylamine which separated from the diluted mixture could be removed by filtration only after standing overnight. Consequently, only a small amount of bisnitronaphthyl disulphide was isolated, which could not be obtained crystalline.

---

* Part IV, *J.*, 1952, 398.

2 : 6-*Dinitronaphthalene.* After removal of precipitated 6-nitro-2-naphthylamine the filtrate was acidified, and the nitronaphthyl sulphide collected, redissolved in aqueous sodium hydroxide, and allowed to oxidise in the air. The *bis*-(6-*nitro*-2-*naphthyl*) *disulphide* when crystallised from hot acetic acid had m. p. 264° (decomp.) (Found : S, 15·8. $C_{20}H_{12}O_4N_2S_2$ requires S, 15·7%).

The authors thank the Department of Scientific and Industrial Research for a maintenance grant (to T. M. C.), Genatosan Ltd. for a maintenance grant (to J. G. H.), and Imperial Chemical Industries Limited, Dyestuffs Division, for gifts of chemicals.

LEICESTER COLLEGE OF TECHNOLOGY AND COMMERCE,
LEICESTER. [*Received, March* 29*th*, 1954.]

The Nitration of β-Nitronaphthalene.

By E. R. WARD and J. G. HAWKINS.

[Reprint Order No. 5345.]

BY nitration of β-nitronaphthalene in acetic acid with fuming nitric acid and sulphuric acid Vesely and Jakes (*Bull. Soc. chim.*, 1923, **33**, 952) obtained a mixture of dinitronaphthalenes. From this they claimed to have separated 1 : 6- and a minute amount of 1 : 7-dinitronaphthalene by crystallisation procedures. By nitration in sulphuric acid only they obtained mixed dinitronaphthalenes and 1 : 3 : 8-trinitronaphthalene. In all cases the polynitro-compounds were identified with authentic specimens. We have re-investigated these nitrations, but like Dean (Thesis, London, 1952) we could not separate pure 1 : 6-dinitronaphthalene from the nitration products by crystallisation. However, examination of the product obtained by nitration in sulphuric acid by means of its infra-red absorption spectrum in the region 8—15 μ established the presence of 1 : 6- (42 ± 5%) and 1 : 7-dinitronaphthalene (52 ± 5%) and 1 : 3 : 8-trinitronaphthalene (9 ± 5%) (the infra-red spectra of all known polynitronaphthalenes, have been surveyed by Whiffen, Hawkins, and Ward, unpublished work). Other known trinitronaphthalenes appeared to be absent.

The product from similar nitration of α-nitronaphthalene contained 1 : 8- (69 ± 5%) and 1 : 5-dinitronaphthalene (31 ± 5%) and some trinitronaphthalenes. Fierz-David and Sponagel (*Helv. Chim. Acta*, 1943, **26**, 98) reported that nitration at −55° afforded a 78 : 22 mixture of these dinitronaphthalenes together with some 1 : 3 : 8-trinitronaphthalene.

Experimental.—α-Nitronaphthalene (2 g.; m. p. 56°) or β-nitronaphthalene (2 g.; m. p. 75·5°) was dissolved in sulphuric acid (*d*, 1·84; 16 c.c.) and treated very slowly, with vigorous stirring, with 4 : 1 (vol.) sulphuric (*d* 1·84)–nitric acid (*d* 1·42) until the dark red solution just became yellow, the temperature being kept at 0°. The mixture was poured on ice and water, and the precipitate collected, washed with much water, and dried for 36 hr. at 55°.

The infra-red spectra were measured, in Nujol mull, on a Grubb-Parsons spectrometer with a sodium chloride prism. For the quantitative estimation the nitration product obtained from α-nitronaphthalene was examined in the range 710—690 cm.$^{-1}$ and that from β-nitronaphthalene in the range 785—705 cm.$^{-1}$, with an approx. 4% solution in dioxan and a cell of thickness 0·11 mm.

The authors thank Genatosan Ltd. for a maintenance grant (to J. G. H.), Professor H. W. Melville, F.R.S., for facilities for recording the infra-red spectra, Dr. D. H. Whiffen for supervising the measurements and assisting in their interpretation, and Imperial Chemical Industries Limited, Dyestuffs Division, for gifts of chemicals.

LEICESTER COLLEGE OF TECHNOLOGY AND COMMERCE, LEICESTER. [*Received, May* 1*st*, 1954.]

A Synthesis of (—)-β-Amino-γ-methylvaleric Acid [(—)-β-*Leucine*].

By K. BALENOVIĆ and D. DVORNIK.

[Reprint Order No. 5277.]

INACTIVE β-leucine has recently been prepared by Birkhofer and Storch (*Chem. Ber.*, 1953, **86**, 529) by hydrolysis of dihydro-4-*iso*propyluracil with hydrochloric acid.

By application of the Arndt–Eistert reaction to (—)-1-diazo-4-methyl-3-phthalimidopentan-2-one prepared from D-valine (cf. *Experientia*, 1947, **3**, 369), (—)-β-amino-γ-methylvaleric acid [(—)-β-leucine] has been obtained in an overall yield of 48% based on D-valine.

Experimental.—M. p.s were determined on a Kofler block.

N-*Phthaloyl*-D-*valine chloride*. *N*-Phthaloyl-D-valine (4·4 g.; $[\alpha]_D$ +68°) (Fling, Minard, and Fox, *J. Amer. Chem. Soc.*, 1947, **69**, 2466) and thionyl chloride (5 c.c.) were heated for 0·5 hr. at 60°; the excess of thionyl chloride was then removed under reduced pressure and the residual crude N-*phthaloyl*-D-*valine* chloride (4·2 g., 89%) was recrystallized from benzene–light petroleum (b. p. 30—50°) giving colourless needles, m. p. 121—122°, $[\alpha]_D^{20}$ —104·0° ± 2° (*c*, 1·0 in C_6H_6) (Found: C, 58·6; H, 4·6. $C_{13}H_{12}O_3NCl$ requires C, 58·8%; H, 4·6%).

The chloride (4·1 g.) was dissolved in ether (45 c.c.) and added to ethereal diazomethane (200 c.c., obtained from 12 g. of nitrosomethylurea). Next morning the solution was filtered and evaporated to dryness under reduced pressure. The residual oily (—)-1-diazo-4-methyl-3-phthalimidopentan-2-one was dissolved in ethyl acetate and precipitated with light petroleum; the oily diazo-ketone was dried *in vacuo* (yield, 3·7 g., 89%) and used without further purification.

Methyl (—)-β-*phthalimido-γ-methylvalerate*. A freshly prepared alkali-free suspension of silver oxide (obtained from 1·5 g. of silver nitrate) was added in four portions during 3 hr. to a refluxing solution of (—)-1-diazo-4-methyl-3-phthalimidopentan-2-one (3·7 g.) in methanol (15 c.c.), and the suspension heated under reflux for a further 4 hr. The hot suspension was treated with charcoal, filtered, and evaporated to dryness. The residue was extracted several times with light petroleum, the solvent from the combined extracts removed under reduced pressure, and the residual oil dissolved in carbon tetrachloride (15 c.c.) and filtered through a column of alumina (8 g.; activity IV). The pale yellow oily *methyl* (—)-β-*phthalimido-γ-methylvalerate* (2·70 g., 72%) obtained after evaporation of the solvent had the b. p. 125—130°/0·01 mm., $[\alpha]_D^{20}$ —6·27° ± 0·5° (*c*, 2·24 in MeOH) (Found: C, 65·5; H, 6·2. $C_{15}H_{17}O_4N$ requires C, 65·4; H, 6·2%).

(—)-β-*Amino-γ-methylvaleric acid* [(—)-β-*leucine*]. A solution of methyl (—)-β-phthalimido-γ-methylvalerate (1·85 g.) in acetic acid (9 c.c.) and 46% hydriodic acid (11 c.c.) was heated under reflux for 10 hr. After cooling, the phthalic acid was filtered off and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in water, the solution extracted with ether (3 × 15 c.c.), and the aqueous layer again evaporated to dryness. The crystalline hydriodide of (—)-β-amino-γ-methylvaleric acid was dissolved in water (700 c.c.) and passed through a column of Amberlite IR-4B (20—50 mesh; 18 g.) at 200 c.c./hr. The column was washed with distilled water (700 c.c.), and the washings were evaporated *in vacuo*. (—)-β-Amino-γ-methylvaleric acid (820 mg., 93·2%) was twice recrystallized from absolute methanol–ether; it then melted at 202—210° (decomp.) and had $[\alpha]_D^{24}$ —39·2° ± 3° (*c*, 0·51 in H_2O), $[\alpha]_D^{20}$ —23·9° ± 1° (*c*, 0·88 in N-HCl), $[\alpha]_D^{20}$ + 4·6° ± 1° (*c*, 0·65 in N-NaOH) (Found: C, 54·7; H, 10·0. Calc. for $C_6H_{13}O_2N$: C, 54·9; H, 10·0%). Birkhofer and Storch (*loc. cit.*) reported m. p. 197—198° for the inactive form.

UNIVERSITY CHEMICAL LABORATORY, STROSMAYEROV TRG 14,
ZAGREB, YUGOSLAVIA.

[*Received, April 3rd*, 1954.]

The Preparation of 2 : 4-Dinitrobenzoic Acid and 2 : 4-Dinitrophenylacetic Acid.

By Jean P. Blanchard and Harlan L. Goering.

[Reprint Order No. 5339.]

In connection with another problem we have recently repeated a synthesis described by Brown and Campbell (*J.*, 1937, 1699) as an improved method for the preparation of 2 : 4-dinitrobenzoic acid. This method involves treating phenylacetic acid with fuming nitric acid and refluxing the resulting solution for 1 hr. Using this procedure we obtained a product in 66% yield (calculated as 2 : 4-dinitrobenzoic acid), which after recrystallization melted at 182·8—184° (Brown and Campbell, *loc. cit.*, report a 70% yield of material which after purification melted at 181—182°). This product, however, has a neutralisation equiv. of 228 corresponding to 2 : 4-dinitrophenylacetic acid (equiv., 226) rather than 2 : 4-dinitrobenzoic acid (equiv., 212). Moreover, the melting point of our material was depressed by authentic 2 : 4-dinitrobenzoic acid (m. p. 182·5—183·5°; equiv., 214) prepared by the chromic acid oxidation of 2 : 4-dinitrotoluene (Buehler and Calfee, *Ind. Eng. Chem. Anal.*, 1934, **6**, 351).

This evidence indicates that the product is 2 : 4-dinitrophenylacetic acid rather than the alleged 2 : 4-dinitrobenzoic acid. This was confirmed by chemical analysis (Found : C, 42·7; H, 2·6; N, 12·7. Calc. for $C_8H_6O_6N_2$: C, 42·5; H, 2·7; N, 12·4%) and by decarboxylation to 2 : 4-dinitrotoluene, m. p. and mixed m. p. 70—71° according to previously described procedures (Radziszewski, *Ber.*, 1870, **3**, 648; Gabriel and Meyer, *Ber.*, 1881, **14**, 823; Borsche, *Ber.*, 1909, **42**, 1310).

University of Wisconsin, Madison 6, Wis., U.S.A. [*Received, April 29th*, 1954.]

---

2 : 3-*Diaminoanisole.*

By E. S. Lane and C. Williams.

[Reprint Order No. 5388.]

A convenient preparation of 2 : 3 diaminoanisole or phenetole was required in connection with the syntheses of new complexing agents for metals. Literature methods for the preparation of the corresponding dinitro-compounds, the reduction of which has provided the most direct route to these compounds, all require difficult isomer separations at some intermediate stage or use inconveniently large quantities of reagents (Easley and Sullivan, *J. Amer. Chem. Soc.*, 1952, **74**, 4450; Holleman, *Rec. Trav. chim.*, 1903, **22**, 271; Blanksma, *ibid.*, 1908, **27**, 49; Verkade and Witjens, *ibid.*, 1946, **65**, 361). A route to 2 : 3-diaminoanisole from *o*-anisidine was therefore investigated.

N-Nitration of *o*-anisidine in potassium ethoxide solution was carried out by a modification of Bamberger's preparation of aryl nitramines (*Ber.*, 1920, **53**, *B*, 2321), the more easily handled amyl nitrate being used in place of ethyl nitrate. The potassium salt of the nitramine was then caused to rearrange in sulphuric acid at −30°, and vacuum distillation then led to a simple separation of the main product, 3-nitro-*o*-anisidine, from the 5-isomer. 2 : 3-Diaminoanisole was obtained by catalytic reduction with hydrogen in approximately 29% overall yield. We have found this route (Brit. Patent Appln. 12710/1954) quicker, more convenient, and less expensive than those described in the literature.

Experimental.—3-*Nitro*-o-*anisidine*. Potassium (45 g.) was dissolved in ethanol (150 ml.) in a nitrogen atmosphere, the solution cooled to 30°, and ether (184 ml.) added with stirring. Whilst the mixture was kept at −10°, amyl nitrate (151 ml.) was added and the mixture stirred for 15 min. *o*-Anisidine (128 ml.) was added in one portion, and the temperature then allowed to rise. The potassium salt of *o*-methoxyphenylnitramine was collected, washed with ether, air-dried (150 g.), and then added portionwise to concentrated sulphuric acid (240 ml.) and water (160 ml.) at −30°. The reaction mixture was left overnight, then poured into water (3 l.), and neutralised with ammonia solution (*d*, 0·88), and the precipitate collected, washed, dried, and distilled. 3-Nitro-*o*-anisidine (61 g., 32%) distilled at 136—140°/0·5 mm. followed by 5-nitro-*o*-anisidine (19 g., 15%) (m. p. 139—140°). Above 230° a vigorous exothermic decomposition of the residual tar occurred. 3-Nitro-*o*-anisidine formed scarlet needles, m. p. 75° (methanol). Bantlin (*Ber.*, 1878, **11**, 2106) recorded m. p. 76°; Ingold and Ingold (*J.*, 1926, 1318) obtained m. p. 75—76° and m. p. 139—140° for the 3- and the 5-isomer, respectively. Acetylation of 3-nitro-*o*-anisidine with acetyl chloride–acetic anhydride gave the *diacetyl* derivative as very pale yellow needles, m. p. 129° (ethanol) (Found : C, 52·1; H, 4·6; N, 11·1. $C_{11}H_{12}O_5N_2$ requires : C, 52·4; H, 4·8; N, 11·1%). This is probably the compound described as the "acetate," m. p. 128°, by Blanksma (*Chem. Zentr.*, 1908, II, 1826); 3-nitroacet-*o*-anisidide, prepared by an unequivocal route by Ingold and Ingold (*loc. cit.*), had m. p. 158—159°.

2 : 3-*Diaminoanisole*. A mixture of 3-nitro-*o*-anisidine (250 g.), Raney nickel (50 g.), and ethanol (750 ml.) was shaken with hydrogen in a stainless-steel autoclave at 100 atm. pressure. The theoretical amount of hydrogen was absorbed during 1 hr. and the temperature rose to 120°. After cooling, the alcoholic solution was filtered, the Raney nickel twice washed with hot ethanol, and the combined solution concentrated. The residue was distilled, 2 : 3-*diaminoanisole* (b. p. 114—116°/0·5 mm.; yield 85—92%) showing a pronounced tendency to remain supercooled. Crystallisation was induced by seeding; the solid had m. p. 35—36° and darkened on exposure (Found: C, 60·3; H, 6·95; N, 20·6. $C_7H_{10}ON_2$ requires C, 60·8; H, 7·25; N, 20·3%). It was characterised as the dihydrochloride, m. p. 246° (water) (Found : C, 39·9; H, 5·6; N, 13·4; Cl, 33·9. Calc. for $C_7H_{12}ON_2Cl_2$: C, 39·8; H, 5·7; N, 13·3; Cl, 33·6%). Wrede and Strack (*Ber.*, 1929, **62**, 2051) record m. p. 250°. 2 : 3-*Dibenzamidoanisole*, white needles, melted at 185° (ethylene glycol) (Found: C, 72·7; H, 5·35; N, 8·0. $C_{21}H_{18}O_3N_2$ requires C, 72·8; H, 5·2; N, 8·1%).

The amino-groups were shown to be vicinal and an indication of the purity of the distillate was obtained by its conversion into 4-*methoxybenzo*-2 : 1 : 3-*selenadiazole* in over 95% yield by reaction of a solution of the amine in dilute hydrochloric acid with selenious acid. This formed yellow needles, m. p. 124—125° (ethanol) (Found : C, 39·3; H, 3·15; N, 13·3. $C_7H_6ON_2Se$ requires C, 39·4; H, 2·8; N, 13·1%).

We are indebted to Dr. I. G. M. Campbell (Southampton University) who suggested the possible value of the nitramine rearrangement for the preparation of *o*-nitro-amines, and to the Director, Chemical Research Laboratories, Teddington, for the provision of hydrogenation facilities.

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, NEAR DIDCOT, BERKS.

[*Received, May* 15*th*, 1954.]