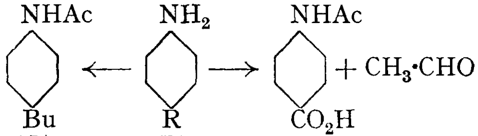
436. *Reactions of Unsaturated Compounds. Part III. Addition of Arylamines to Butadiene.*

By W. J. Hickinbottom.

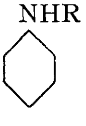
The behaviour of butadiene towards aniline and *p*-toluidine presents several features of interest. It is well known that Δ^{α}-unsaturated ketones, acids, and esters containing conjugated linkages combine additively with ammonia and primary and secondary amines to furnish β-amino-ketones, -acids, and -esters (Blank, *Ber.*, 1895, **28**, 145; Goldstein, *ibid.*, p. 1450; 1896, **29**, 813; E. Fischer and Scheibler, *Annalen*, 1911, **383**, 339; Stoermer and Robert, *Ber.*, 1922, **55**, 1030; Tambor and Wildi, *Ber.*, 1898, **31**, 349; Morsch, *Monatsh.*, 1932, **60**, 50). Butadiene does not behave in this manner, for even when heated with aniline at 260° for 24 hours it merely polymerises and the aniline is recovered unchanged. It appears to be a legitimate inference from this result that the saturation of the double bond of Δ^{α}-unsaturated ketones and esters by amines is not primarily dependent on the conjugated system of double bonds. The determining factor would appear to be the carbonyl group, which is known to react with amines under certain conditions. This, coupled with a suitable disposition of the double bond, serves to complete the reaction (compare Lapworth and McRae, J., 1922, **121**, 2742; Kolker and Lapworth, J., 1925, **127**, 309).

Another conclusion is that, in spite of the activating influence of the amino-group on nuclear substitution, it appears to be unable to promote the fusion of butadiene with the aromatic nucleus in the manner of the diene syntheses described by Diels and Alder (1928—1932).

Aniline and butadiene react at 240—260° in presence of aniline hydrochloride or hydrobromide. The principal products are α-*p*-*aminophenyl*-Δ^{β}-*butene* and α-anilino-Δ^{β}-butene (I and III respectively; R = $CH_2{\cdot}CH{:}CHMe$). α-*p*-Aminophenyl-Δ^{β}-butene yields a crystalline *hydrochloride* and a sparingly soluble *sulphate*; its salts are diazotised normally in aqueous mineral acid solution. The *acetyl* derivative of (I) combines additively with bromine to form a crystalline *dibromide*. On hydrogenation it takes up two atoms of hydrogen; the product is *p*-acetamido-*n*-butylbenzene (II), thereby establishing that the aminoaryl group is attached to the terminal atom of the butenyl group. Oxidation of the acetyl derivative of (I) with permanganate yields acetaldehyde, a result which is only consistent with the double bond being situated between the β- and the γ-carbon atom. Further oxidation of the acetyl derivative furnishes *p*-acetamidobenzoic acid, thus confirming the orientation of the amino-group with respect to the side chain.



(II.) (I.)



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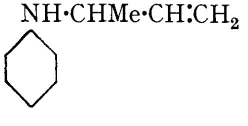

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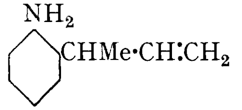

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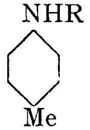
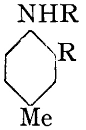


(VI.)



(VII.)

[R = $CH_2{\cdot}CH{:}CHMe$.]

The amine (III) was purified through its *nitrosoamine*. The structure assigned to the amine depends on the formation of acetaldehyde when its *acetyl* derivative is oxidised with permanganate. Hydrogenation of the amine or its acetyl derivative did not give satisfactory results owing to the comparatively slow absorption of hydrogen.

During the reaction between butadiene and aniline in the presence of a suitable catalyst, other products are formed in amounts depending on the experimental conditions. They consist of mono- and di-secondary, di-primary, and mixed primary secondary amines resulting from the further condensation of aniline and butadiene with the primary products (I) and (III), but cannot be separated in a pure state owing to similarity in boiling point and the absence of suitable crystalline derivatives.

A less complex result is obtained when *p*-toluidine is heated with butadiene in presence of *p*-toluidine hydrochloride. The main products are *α-p-toluidino-Δ^{β}-butene* (VI) and *4-butenylamino-3-butenyltoluene* (VII).

The main reaction of butadiene with aniline or *p*-toluidine in presence of a suitable catalyst is therefore substitution in the amino-group or in the aromatic nucleus with the formation of primary and secondary amines. It follows, therefore, the general behaviour of arylamines with simple olefins (J., 1932, 2646; this vol., p. 319), and this may now be considered the normal behaviour of an unsaturated hydrocarbon when heated with aniline and aniline hydrochloride.

In addition to the products already mentioned, the reactions described furnish small amounts of indole derivatives. Thus from aniline, aniline hydrochloride, and butadiene, 2 : 3-dimethylindole is formed, the yield being approximately 0·4% of the theoretical; *p*-toluidine furnishes 2 : 3 : 5-trimethylindole in about 2% yield. The formation of indoles is of interest in that it appears to be an example of ring formation in which butadiene reacts in the βγ-position. In all the hitherto recorded cases of ring formation by the combination of butadiene with suitably constituted compounds, reaction occurs in the αδ-position (compare Alder, " Methoden der Dien-synthese," 1933). The examples now recorded, however, differ from the normal Diels–Alder diene syntheses in that a catalyst is necessary to bring about combination and that ring formation is accompanied by dehydrogenation. It would appear not improbable that the formation of dimethylindole depends on the intermediate production of either (IV) or (V), which cyclises owing to a suitable disposition of the double bond in the side chain. The resulting dihydroindole then suffers dehydrogenation to dimethylindole.

EXPERIMENTAL.

Reaction of Aniline with Butadiene.—The usual procedure consisted in heating a solution of butadiene in aniline (approx. 8—12% concn.) with aniline hydrochloride or hydrobromide in a sealed tube at 220—260° for 4—25 hours. The following table gives particulars of some of the preparations.

						Yields, g.*			
$PhNH_2$, g.	C_4H_6, g.	Catalyst.	Wt, g.	Temp.	Hrs.	(I).	(III).	Complex products.	Dimethyl-indole.
85	7·7	$PhNH_2$,HBr	4	230—260°	4	2·21	1·20	4·35	—
80	6·0	$PhNH_2$,HCl	2	220—245	25	1·03	0·37	1·26	0·061
100	8·0	$PhNH_2$,HCl	2	235	24	1·84	1·02	1·84	0·067
64	9·5	$PhNH_2$,HBr	4	250	5	3·0	1·54	—	—

* The yields of anilinobutene, *p*-aminophenylbutene, and dimethylindole are those of the pure products.

The product was dissolved in a moderate excess of 3*N*-hydrochloric acid, slightly basic and neutral substances (A) were extracted in ether, the aqueous solution was rendered alkaline, and the liberated amines were taken up in ether. After drying, this ethereal solution was fractionated, first at atmospheric pressure to remove the solvent and the bulk of the aniline, then under reduced pressure. The main fractions were collected at 100—160°/25 mm. and 160—250°/25 mm. The dark viscous residue was not examined.

Isolation of **α-p-*aminophenyl-Δ^{β}-butene*.** The fraction, b. p. 100—160°/25 mm., was treated with a slight excess of *N*-sulphuric acid (Congo-paper), and the sparingly soluble sulphate was collected (filtrate B), washed with ether, and crystallised from hot water, yielding pure *α-p-aminophenyl-Δ^{β}-butene sulphate* in white scales [Found : H_2SO_4, 25·4. $(C_{10}H_{13}N)_2,H_2SO_4$ requires H_2SO_4, 25·0%].

The *amine* liberated from the sulphate by the action of aqueous ammonia was a colourless oil, b. p. 135—136°/24 mm. (Found : C, 82·0; H, 8·7. $C_{10}H_{13}N$ requires C, 81·6; H, 8·9%), having an odour resembling that of the *p*-amino-*n*-alkylbenzenes. The *hydrochloride* separated from hot ethyl acetate containing some ethyl alcohol as silky needles, which, when moist, turned brown on keeping (Found : HCl, 20·3. $C_{10}H_{13}N$,HCl requires HCl, 19·9%). After diazotisation with aqueous sodium nitrite, the product coupled with β-naphthol in alkaline solution to yield an *azo-β-naphthol*, slender, brilliant red needles (from glacial acetic acid), m. p. 100—101° (Found : N, 9·3. $C_{20}H_{18}ON_2$ requires N, 9·2%).

Acetylation of the amine with an aqueous suspension of acetic anhydride gave *α-*p*-acetamidophenyl-Δ^β-butene*, small platelets (from aqueous alcohol), m. p. 98—99° (Found : C, 76·3; H, 8·0; N, 7·3. $C_{12}H_{15}ON$ requires C, 76·1; H, 8·0; N, 7·4%). The acetyl compound decolorised bromine in chloroform, and after evaporation of the solvent and crystallisation of the residue from alcohol *βγ-dibromo-α-*p*-acetamidophenylbutane* was obtained in white platelets, m. p. 127—128° (Found : C, 41·3; H, 4·4; N, 4·1; Br, 45·9. $C_{12}H_{15}ONBr_2$ requires C, 41·3; H, 4·3; N, 4·0; Br, 45·8%).

Hydrogenation of α-*p*-acetamidophenyl-Δ^β-butene in glacial acetic acid with colloidal palladium as catalyst yielded *p*-acetamido-*n*-butylbenzene (0·457 g. absorbed 57·9 c.c. of hydrogen at N.T.P. Theory, 54·1 c.c.), m. p. and mixed m. p. 103—104° (Reilly and Hickinbottom, J., 1920, **117**, 111).

Oxidation of α-*p*-acetamidophenyl-Δ^β-butene was effected by adding 0·5% aqueous permanganate (about 150 c.c.) to a solution of the acetyl derivative (0·47 g. in 10 c.c. of glacial acetic acid diluted with 10 c.c. of 5*N*-acetic acid). The colour of the permanganate was rapidly discharged. The solution was distilled to remove the volatile products of oxidation, cooled, treated with a further amount of permanganate (100 c.c.), and again distilled. These operations were repeated until about 500 c.c. of permanganate had been added. The distillate responded to Schiff's test for an aldehyde and gave with 2 : 4-dinitrophenylhydrazine a precipitate of acetaldehyde-2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 164—166° (Found : C, 43·0; H, 3·4; N, 25·1. Calc. : C, 42·9; H, 3·6; N, 25·0%). The identity was confirmed crystallographically by Mr. E. G. Cox.

From the aqueous solution containing the non-volatile products of the oxidation, *p*-acetamidobenzoic acid, m. p. 254—256° (decomp.), was isolated; it was identified by mixed m. p. and crystallographically.

Isolation of α-anilino-Δ^β-butene. The filtrate (B) (p. 1982) was made alkaline, and the liberated amine taken up in ether. After washing and drying (magnesium sulphate), the solvent was evaporated and the residual amines were treated with 50% aqueous zinc chloride. The sparingly soluble zincichlorides (C) were collected after 12 hours, washed with water, and extracted several times with boiling light petroleum. The residue consisted essentially of the zincichlorides of aniline and *p*-aminophenylbutene. The light petroleum extract was fractionated and the distillate collected between 130° and 140°/33 mm. was shaken with several successive quantities of 3*N*-hydrochloric acid. The acid solution, treated with a slight excess of sodium nitrite, became orange-red, and a nitrosoamine separated as an oil, which was removed in ether. The aqueous solution now became green on addition of an excess of ammonia, indicating the presence of a tertiary amine; the quantity, however, was too small for isolation.

The nitrosoamine was washed in the ethereal solution with water and then several times with dilute alkali before being distilled in steam. *Phenylbutenylnitrosoamine* was obtained as a pale yellow oil with a characteristic rooty odour, quite distinct from that of phenyl-*n*-butylnitrosoamine. For analysis, a portion was stored over concentrated sulphuric acid in a vacuum desiccator (Found : C, 68·3; H, 7·4. $C_{10}H_{12}ON_2$ requires C, 68·1; H, 6·9%). The nitrosoamine formed in cold concentrated sulphuric acid a deep cherry-red solution, which became yellowish-brown on dilution. The cherry-red solution changed through green to deep indigo-blue on addition of phenol and warming. This solution, on dilution with water, became cherry-red, purple, and finally brownish-red. A greenish-blue colour resulted on addition of an excess of alkali.

The nitrosoamine was converted by Kenner and Jones's method (J., 1932, 713) into α-anilino-Δ^β-butene, a colourless liquid, b. p 132—134°/34 mm. The *acetyl* derivative was a viscous liquid, b. p. 165—168°/28 mm. (Found : C, 76·1; H, 8·1. $C_{12}H_{15}ON$ requires C, 76·1; H, 8·0%). It combined with bromine in chloroform comparatively slowly, and hydrogenation in glacial acetic acid with a palladium catalyst also was comparatively slow, not being complete after 15 hours (0·5378 g. absorbed 17 c.c. Theory, 64 c.c.). Oxidation of the acetyl compound in aqueous acetic acid with permanganate furnished acetaldehyde (2 : 4-dinitrophenylhydrazone), identified crystallographically and by mixed m. p.

Isolation of 2 : 3-*dimethylindole.* The neutral and the feebly basic products (A) (p. 1982) were distilled under reduced pressure, giving a main fraction, b. p. 150—180°/33 mm., which consisted largely of diphenylamine, the bulk of which crystallised and was removed. The liquid portion was diluted with ether and washed with a mixture of concentrated hydrochloric acid (1 vol.) and 3*N*-hydrochloric acid (½ vol.). The ethereal solution was then washed with water, dried, and evaporated, yielding crude dimethylindole. This was purified through its picrate, reddish-brown needles, m. p. and mixed m. p. 154—155° (Wolff, *Ber.*, 1888, **21**, 125, gives m. p. 157°). Treatment of the pure picrate with aqueous ammonia, followed by steam distillation, yielded 2 : 3-dimethylindole, thin plates (from light petroleum), m. p. 105—106°. The identity was established by analysis (Found : C, 82·25; H, 7·45; N, 9·7. Calc. : C, 82·7; H, 7·6; N, 9·7%), and by comparison (mixed m. p. and solubilities) with a genuine specimen prepared by Fischer's method (*Annalen*, 1886, **236**, 128).

Reaction of p-*Toluidine with Butadiene.*—Benzene solutions of butadiene were heated with an excess of *p*-toluidine and some *p*-toluidine hydrochloride in sealed tubes.

C_4H_6, g.	*p*-$C_7H_7{\cdot}NH_2$, g.	$C_7H_7{\cdot}NH_2$,HCl, g.	Temp.	Hrs.	Yields, g. Trimethylindole.	(VI).	(VII).
5	60	2	240°	24	0·135	0·61	0·72
5	88	6	225	24	0·296	0·31	—
5	60	12	230	24	0·24	1·41	1·54

A preliminary separation into basic and feebly basic material was effected by treatment with dilute hydrochloric acid and ether in the manner described on p. 1982.

Isolation of α-p-*toluidino*-Δ^β-*butene and* 4-*butenylamino*-3-*butenyltoluene*. The amines were liberated from the dilute acid solution of the basic products by excess of ammonia and fractionated at atmospheric pressure to remove the bulk of *p*-toluidine. Distillation under reduced pressure then gave two main fractions, 135—145°/32 mm. and 175—190°/30 mm.

The lower-boiling fraction consisted essentially of α-p-*toluidino*-Δ^β-*butene*. It was freed from a trace of primary amine by treatment with aqueous zinc chloride and after several distillations under reduced pressure was obtained pure as a very pale straw-yellow liquid, b. p. 135°/33 mm. (Found : C, 81·7; H, 9·4. $C_{11}H_{15}N$ requires C, 81·9; H, 9·4%). The *chloroplatinate* formed slender buff-coloured needles from hot absolute alcohol, m. p. 200—201° (decomp.) [Found : Pt, 26·4. $(C_{11}H_{15}N)_2,H_2PtCl_6$ requires Pt, 26·7%]. The *nitrosoamine*, a yellow oil volatile in steam (Found: C, 69·5; H, 7·6. $C_{11}H_{14}ON_2$ requires C, 69·4; H, 7·4%), dissolved in concentrated sulphuric acid to give a colourless solution which responded to the Liebermann nitroso-test.

The fraction collected between 175° and 190°/30 mm. was dissolved in 3*N*-hydrochloric acid and repeatedly extracted with ether. The amine liberated by alkali was taken up in ether, dried, and distilled, giving a viscous, pale yellow oil, b. p. 185°/30 mm. (Found : C, 83·2; H, 9·8. $C_{15}H_{21}N$ requires C, 83·6; H, 9·8%), which decolorised a cold dilute solution of permanganate fairly rapidly.

The *nitrosoamine* derived from 4-*butenylamino*-3-*butenyltoluene* was a yellow viscous oil, not readily volatile in steam. It was washed with dilute aqueous alkali, distilled in steam, taken up in ether, dried, recovered, and stored over concentrated sulphuric acid in a partial vacuum for several days (Found : C, 73·1; H, 8·4. $C_{15}H_{20}ON_2$ requires C, 73·7; H, 8·3%).

Isolation of 2 : 3 : 5-*trimethylindole*. The neutral and the feebly basic products of the reaction of butadiene with *p*-toluidine (see above) were distilled under reduced pressure. The greater part was collected between 140° and 190°/27 mm.; the tarry residue appeared to consist essentially of polymerised butadiene. The main fraction partly solidified on cooling. It was drained under suction, and the solid residue crystallised from light petroleum, yielding pure di-*p*-tolylamine, m. p. and mixed m. p. 79° (nitrosoamine, m. p. 102°). The more soluble portion of the main fraction was diluted with a large volume of ether and shaken with fairly concentrated hydrochloric acid. The washed and dried ethereal solution was evaporated, and the residue treated with a benzene solution of picric acid. The *picrate* of 2 : 3 : 5-trimethylindole separated. The pure picrate gave a deep red solution in hot benzene and separated on cooling as a mass of dark brown needles, m. p. 188—189° (Found : C, 52·6; H, 4·0; N, 14·1. $C_{11}H_{13}N,C_6H_3O_7N_3$ requires C, 52·6; H, 4·15; N, 14·4%). Trimethylindole liberated from the picrate separated from light petroleum (b. p. 40—60°) as platelets, m. p. 120—121° (Found: C, 83·1; H, 8·6; N, 8·9. Calc. : C, 83·0; H, 8·2; N, 8·8%) [Wolff gives m. p. 121·5° and describes the picrate (no analysis) as brownish-red needles, m. p. 189°]. The general characteristics of the compounds isolated in the present work agree with those described by Wolff, with the exception that the picrate has been found to be sparingly soluble in cold benzene.

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