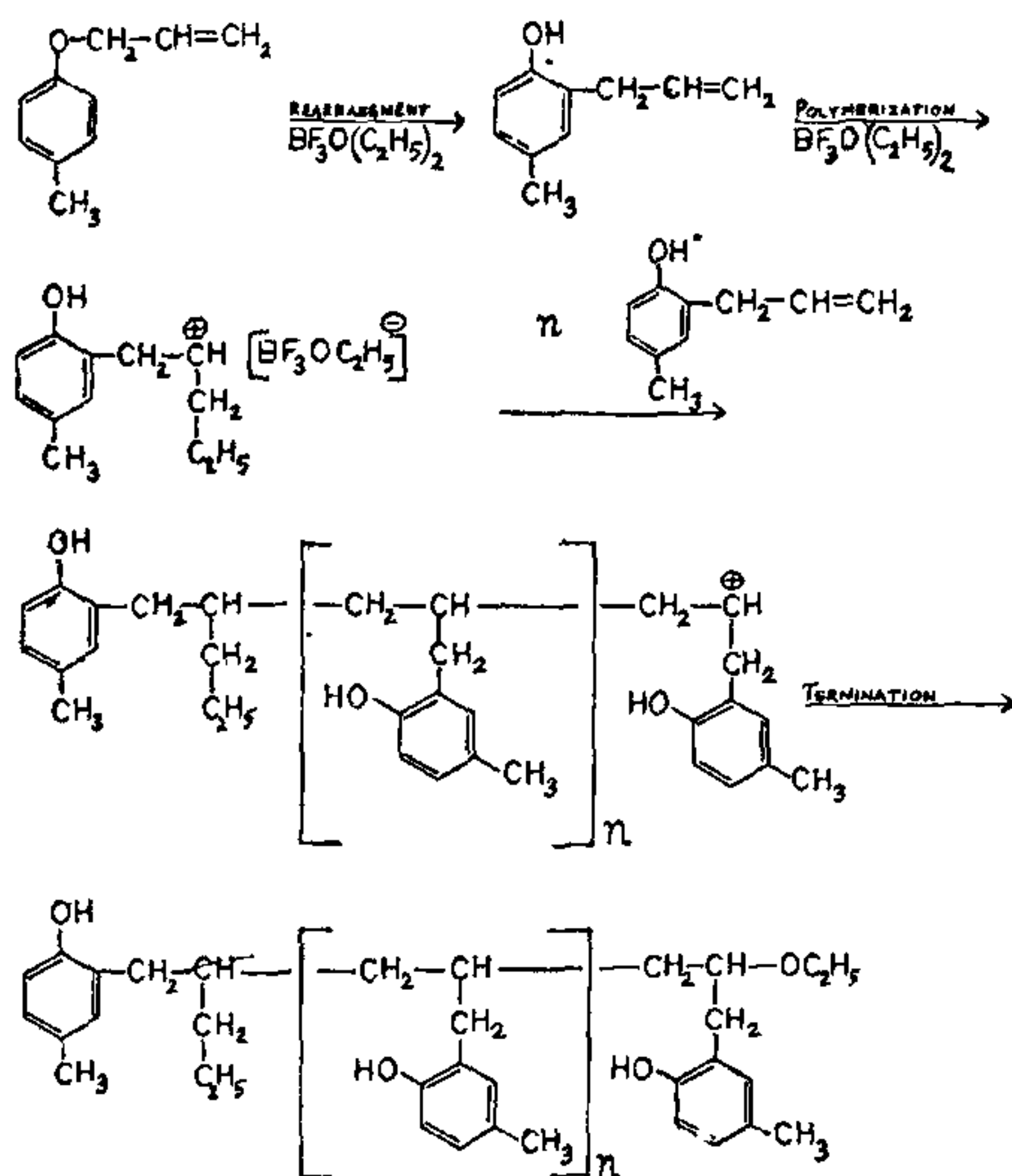


polymerize with boron trifluoride dietherate. This is understandable as both the ortho and the para position are blocked by bromine atoms preventing rearrangement.



In contradistinction, allyl-4-methyl phenyl ether was readily polymerized by boron trifluoride dietherate at room temperature. The IR spectrum of the purified polymer indicated the characteristic phenolic -OH vibrational frequencies at 3100-3600 cm^{-1} . The absence of unsaturation was also indicated by the PMR spectrum which showed no peak around 5-6.32 δ . The polymer decomposed at 432° K as observed in a differential scanning calorimeter. Thus the polymerization has proceeded through rearrangement.

Since the polymer is structurally different from the atomic arrangement of the monomer molecule, this polymer may be called a "Phantom Polymer"².

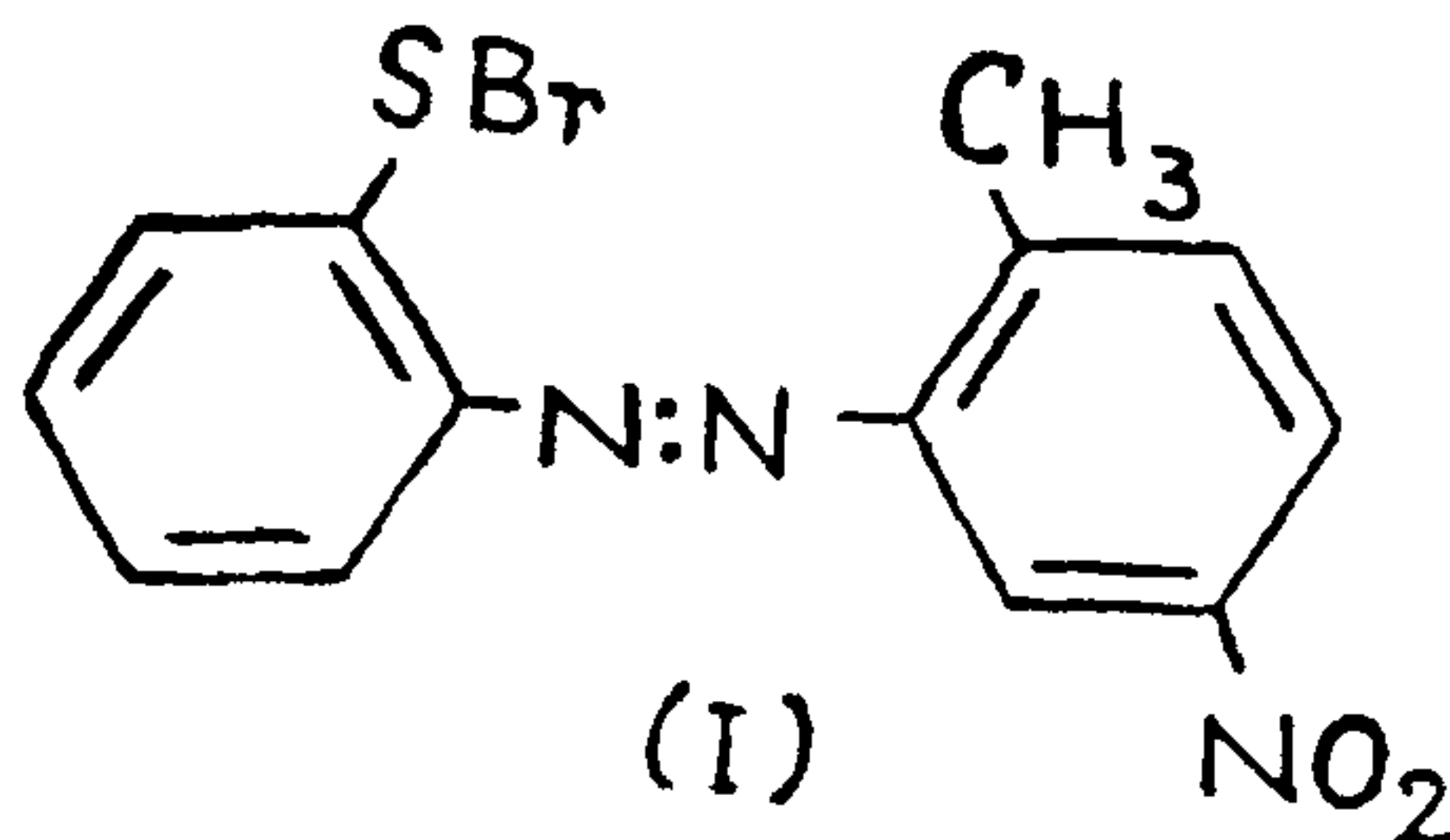
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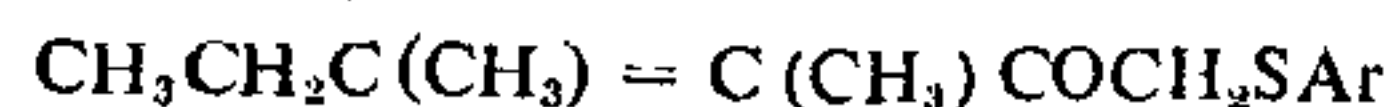
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REACTION OF 2-METHYL-5-NITRO-AZOBENZENE-2'-SULPHENYL BROMIDE WITH ETHYL METHYL KETONE

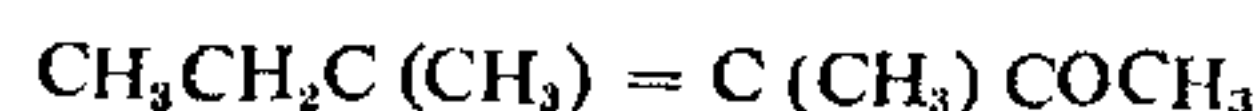
IN earlier work^{1,2} it is reported that in the condensation reactions between the stable aryl sulphenyl bromides and methyl ketones CH_3COR , the active hydrogen necessary for the reaction is available from the methyl group of the methyl ketones. But we have observed that in the reaction between the newly synthesized compound 2-methyl-5-nitro-azobenzene-2' sulphenyl bromide(I)³ and ethyl methyl ketone, the active hydrogen is available from the other side of the keto group, i.e., from the methylene group of the ketone $\text{CH}_3\text{COCH}_2\text{CH}_3$, resulting in the formation of the ketonylsulphide(II) as a minor product. The major product is an $\alpha\beta$ -unsaturated ketonyl-sulphide(II). The hydrobromic acid initially formed due to the condensation of (I) with the ketone yielding (II) may catalyze an aldol condensation of the ketone ultimately resulting in the formation of an $\alpha\beta$ -unsaturated ketone(IV). It is known that in acid catalyzed aldol condensation the active hydrogen is available from the methylene group (and not from the methyl group) of



(II)

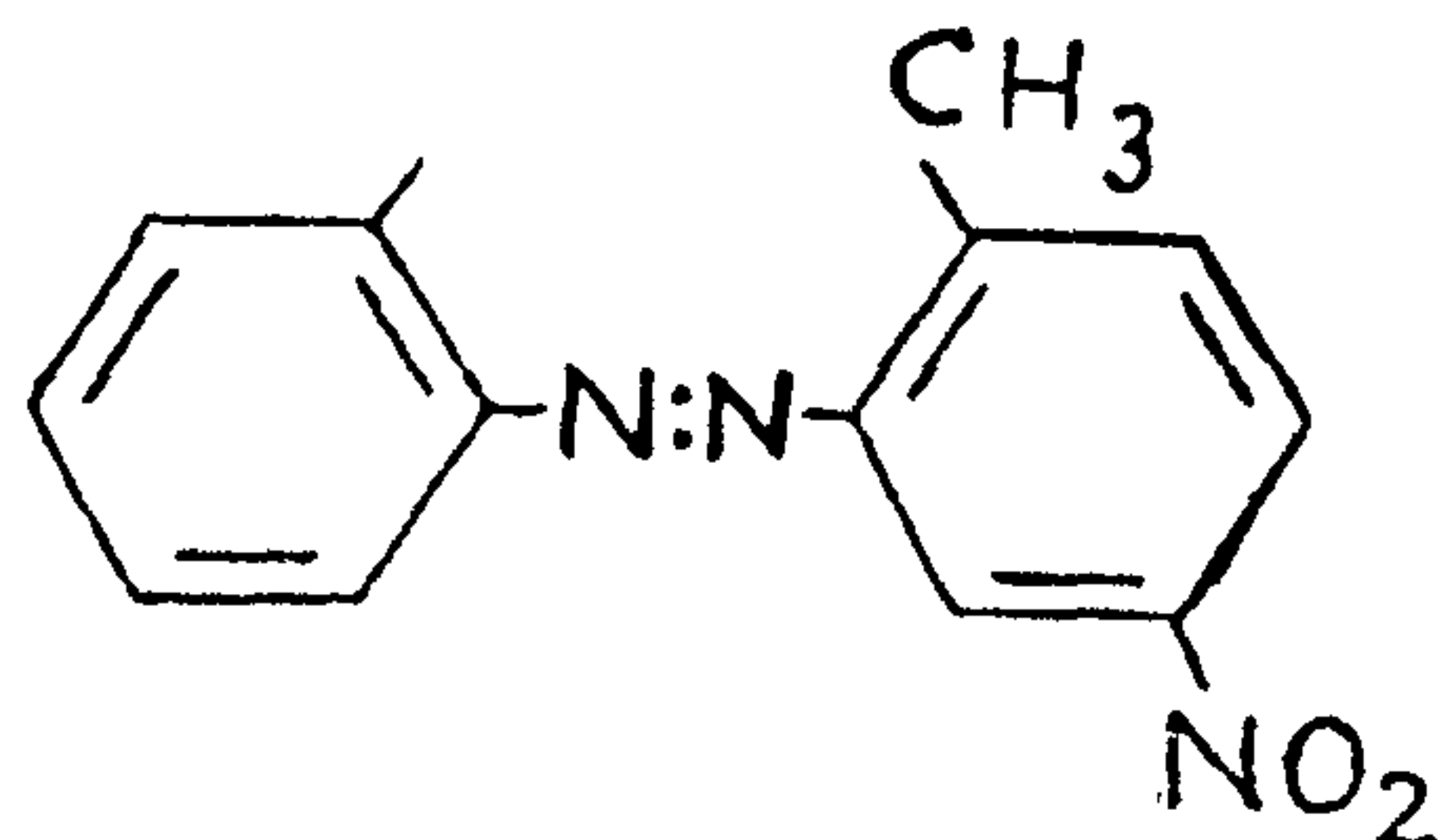


(III)



(IV)

where Ar =



the methyl ketone⁴. So the acid catalyzed condensation product of ethyl methyl ketone will have the structure(IV). The unreacted sulphenyl bromide then reacts with (IV) to give the sulphide(III). The structures attributed to the sulphides(II) and (III) are supported by the elemental and spectral analysis.

Experimental

Reaction of (I) with ethyl methyl ketone. The sulphenyl bromide (0.5 g) was dissolved in ethanol (200 ml) and water (25 ml). To it was added ethyl methyl ketone (3 ml). The mixture was shaken well and kept at room temperature (30 °C) till the reaction was complete (4 days). The mixture was then diluted with water (200 ml) when an orange precipitate was obtained. It was then filtered, washed and dried (0.4 g, m.p. 92°–98° C). It was then dissolved in minimum amount of benzene and poured over a column of active alumina and eluted with 80 : 20 benzene-light petrol (40°–60° C) mixture and different fractions were collected.

The first fraction on evaporation to dryness under reduced pressure gave an orange residue of *o*-(2-methyl-5-nitro-phenylazo)-phenyl, 3-oxo-butyl-2-sulphide(II). This was then crystallized from ethanol as orange needles, m.p. 98° C, yield 75 mg.

(C₁₇H₁₇N₃O₃S requires C = 59.5, H = 5.0, N = 12.2%, found, C = 59.8, H = 5.2, N = 11.9%).

The second fraction on evaporation to dryness under reduced pressure gave a yellow residue. This residue of *o*-(2-methyl-5-nitro-phenylazo)-phenyl, 3,4-dimethyl-5-oxo-hex-3-enyl sulphide(III) was washed with cold ethanol and crystallized from benzene-ethanol mixture as fine yellow needles, m.p. 166° C, yield 170 mg.

(C₂₁H₂₃N₃O₃S requires C = 63.5, H = 5.8, N = 10.6%, found, C = 63.5, H = 5.6, N = 10.6%).

Spectral Analysis

A. Uv and visibles pectra :—Both of the sulphides(II) and (III) display similar spectral pattern in ethanol and benzene having the R-band ($\pi \rightarrow \pi^*$ band) due to the azo group and the K-band ($\pi \rightarrow \pi^*$ band) due to the conjugated arylazo chromophore.

Compound	R-band nm (ϵ)	K-band nm (ϵ)	solvent
(II)	402 (1100)	323 (9000)	benzene
(II)	404 (1200)	320 (10000)	ethanol
(III)	410 (1500)	327 (13700)	benzene
(III)	404 (1500)	323 (14000)	ethanol

B. IR spectra :

Compound	$\nu_{\max}^{\text{nujol}}$ cm ⁻¹
(II)	1715 (strong, C=O stretch), 1600 (weak, N=N stretch)
(III)	1670 (strong, C=C-C=O stretch), 1590 (weak, N=N stretch).

C. NMR spectra :

Compound	τ -values
(II)	8.8 (doublet, 3H, CH ₃ -CH-), 8.4 (singlet, 3H, CH ₃ -CO-) 7.6 (singlet, 3H, CH ₃ - ϕ), 6.9 (quartet, 1H, S-CH-CH ₃) CO 2-3.2 (complex multiplet, 7H, aromatic protons)
(III)	8.9 (triplet, 3H, CH ₃ -CH ₂ -), 8.5 (quartet, 2H, C=C-CH ₂ CH ₃), 8.1 (singlet, 3H, CH ₃ -C=C-), 7.8 (singlet, 3H, CH ₃ -C=C-CO), 7.6 (singlet, 3H, CH ₃ - ϕ), 7.5 (singlet, 2H, S-CH ₂ -CO-), 2-3.3 (complex multiplet, 7H, aromatic protons).

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March 27, 1979. S. K. BHATTACHARJEE.

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CHEMICAL EXAMINATION OF THE STEMS OF LIPPIA CITRIODORA LINN.

Lippia citriodora Linn. (Verbenaceae) is a shrub, indigenous to S. America and commonly grown in gardens in India. The leaves were reported¹ to be useful for flavouring beverages, desserts, fruit salads and jellies, for seasoning food and in the preparation of ptisan and in sachets. A decoction of the leaves and flowers is given as febrifuge, sedative and antifatulent. The leaves and flower tops were reported² to contain an essential oil, commonly known as verbena oil, besides hydrolyzable tannins, acid phenols, flavonoids and alkaloids.

We have examined the stems for chemical constituents by solvent extraction method. From the combined extracts of *n*-hexane and benzene, the following compounds have been separated using column chromatography over silica gel and identified.