The Chemistry of Azidotropones. Part II.[1] 3- and 4-Azidotropones and Related Compounds

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When treated with oxalyl chloride, the sodium salts of 3- and 4-hydroxytropones afford intermediates of uncertain structure, possibly derivatives of ditropyl ether, which are nevertheless converted into the corresponding chlorotropones on hydrolysis. The behaviour of these compounds in some nucleophilic substitution reactions is qualitatively examined; displacement of halogen by azide ion occurs normally, but some *cine*-substitution occurs in the reaction of 3-chlorotropone with dimethylamine. Thermolysis and photolysis of 3- and 4-azidotropones gives the corresponding amino-derivatives as the only isolable products.

THE remarkably ready thermal and photochemical decompositions of 2-azidotropones, in which loss of nitrogen is accompanied by ring cleavage leading to diene-ketens,[1,2] prompted an examination of the behaviour of the 3- and 4-substituted analogues. While direct nucleophilic displacement by azide ion offered the most straightforward preparative approach to these compounds, few tropones bearing a single, easily displaceable 3- or 4-substituent have been described. Moreover, in contrast to the numerous studies of the reactivity of 2-substituted tropones towards anionoid reagents,[3,4] relatively little work on the 3- and 4-isomers has been reported, although the parent tropolones were prepared several years ago.[5,6]

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[1] Part I, J. D. Hobson and J. R. Malpass, *J. Chem. Soc.* (*C*), 1967, 1645.

[2] J. D. Hobson, M. M. Al-Holly, and J. R. Malpass, *Chem. Comm.*, 1968, 764.

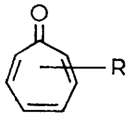
[3] *Inter alia*: P. L. Pauson, *Chem. Rev.*, 1955, **55**, 9. T. Nozoe, *Fortschr. Chem. org. Naturstoffe*, 1956, **13**, 279. T. Nozoe in 'Non-Benzenoid Aromatic Compounds,' ed. D. Ginsburg, Interscience, New York, 1959, p. 339; W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1952, **74**, 5683; W. von E. Doering and C. F. Hiskey, *ibid.*, 1952, **74**, 5688; W. von E. Doering and D. B. Denney, *ibid.*, 1955, **77**, 4619; S. Itô, J. Tsunetsugu, T. Kanno, H. Sugiyama, and H. Takishita, *Tetrahedron Letters*, 1965, 3659; T. Asao and M. Kobayashi, *Bull. Chem. Soc. Japan*, 1966, **39**, 2538. T. Sato, *J. Chem. Soc. Japan*, 1959, **80**, 1167; 1967, **88**, 355.

[4] D. G. Lloyd, 'Carbocyclic non-Benzenoid Aromatic Compounds,' Elsevier, London, 1966, ch. 6.

[5] R. B. Johns, A. W. Johnson, and M. Tisler, *J. Chem. Soc.*, 1954, 4605; R. S. Coffey and A. W. Johnson, *ibid.*, 1958, 1741; A. J. Birch, J. M. H. Graves, and F. Stansfield, *Proc. Chem. Soc.*, 1962, 282.

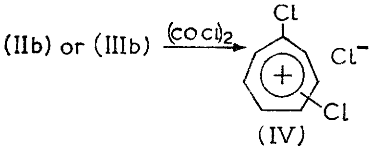
[6] (*a*) O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.*, 1963, **85**, 41; (*b*) O. L. Chapman and J. Meinwald, *ibid.*, 1958, **80**, 633.

The toluene-*p*-sulphonate of 3-hydroxytropone (IIa) though recently reported to undergo ammonolysis to the 3-amino-compound,[7] proved to be an unsuitable precursor for the azide (IIc); the only isolable product from its reaction with sodium azide was toluene-*p*-sulphonamide. The chlorotropones (IIb) and (IIIb) also appeared to be quite inaccessible *via* the reaction of thionyl chloride with the corresponding tropolones (IIa) and (IIIa); * only tar was produced, and, in the case of the 3-isomer, a small amount of a dichlorobenzaldehyde. Treatment of the dry sodium salt of 3-hydroxytropone with oxalyl chloride gave (IIb), but the reaction showed some complexities, and good yields were obtained only by the use of excess of reagent followed by an aqueous work-up. The primary product, isolated under anhydrous conditions, was a mobile hygroscopic oil, $\nu_{max.}$ 1605 cm.$^{-1}$, showing only a complex group of n.m.r. signals at τ 3·6—4·2, *i.e.* at notably higher field than the signals for (IIb) itself. It was rapidly transformed by atmospheric moisture first into a crystalline solid, then into an oil, from which 3-chlorotropone was isolated as a low-melting hemihydrate.

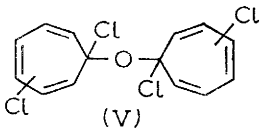


(I; 2-substituent)
(II; 3-substituent)
(III; 4-substituent)

a; R = OH. b; R = Cl. c; R = N_3. d; R = NH_2.
e; R = NMe_2



(IV)



(V)

The reaction of the sodium salt of 4-hydroxytropone (IIIa) followed a similar course. The immediate product was a non-troponoid oil with spectra very similar to those of the material obtained from the 3-isomer. Hydrolysis with water was accompanied by pronounced changes in spectroscopic properties, including a downfield shift of the n.m.r. absorption, resulting from the formation of the 4-chloro-compound (IIIb), which was, in this case, a non-hygroscopic, crystalline material.

The nature of the oily unsaturated precursors of the chlorotropones is uncertain, and their instability in the atmosphere hindered detailed study. The same materials were generated when the chlorotropones themselves were treated with oxalyl chloride in benzene, a reaction which might reasonably be expected to lead initially to the corresponding 1,3- or 1,4-dichlorotropylium chlorides (IV). The inference that the intermediates were derived from the latter was supported by their mass spectra, both of which showed the intense peaks at *m/e* 163, 161, and 159 (intensity ratios 1 : 6 : 9) expected for a dichlorotropylium ion (IV). The presence also of M^+ and $(M - CO)^+$ peaks characteristic of the corresponding chlorotropones suggested that these products may result from a combination of the chlorotropone with the corresponding dichlorotropylium chloride (IV), dissociation into these two components occurring upon electron impact. A ditropyl ether formulation, *e.g.* (V), might account for these observations, but neither mass spectrum showed ant appropriate M^+ peaks, and the suggestion remains only tentative.

With sodium azide in dimethyl sulphoxide, both 3- and 4-chlorotropones underwent nucleophilic substitution under mild conditions, quantitatively affording the corresponding azido-compounds (IIc) and (IIIc). These were characterised by their spectra and by conversion into the corresponding amino-compounds (IId) and (IIId) by catalytic reduction, and thence into the tropolones (IIa) and (IIIa) by alkaline hydrolysis.

In contrast to the behaviour of the 2-isomer,[1] 3- and 4-azidotropones were relatively thermostable, and rapid evolution of nitrogen from solutions in inert solvents occurred only at temperatures greater than 140°. The products from thermolysis and photolysis experiments on these two azides were apparently largely intractable polymeric materials, from which only small yields of the corresponding aminotropones were isolated.

The uncomplicated behaviour of 3- and 4-aminotropones towards aqueous alkali, shown also by the 2-amino-isomer,[8] contrasts with that of the chlorotropones. In the case of 2-chlorotropone, direct displacement leading to tropolone is not observed, and nucleophilic addition to the carbonyl group apparently competes with attack at the 3-position, both reactions resulting in ring-contraction to give benzenoid products.[9] However, the 3- and 4-chloro-compounds (IIb) and (IIIb) were rapidly converted by mild alkali into intractable tar and, as with the 2-isomer, only acid-catalysed hydrolysis regenerated the corresponding tropolones. In the event that base-catalysed tropone ring contraction occurs in these cases, the chlorine substituent may well be unfavourably situated for subsequent easy elimination, with the result that unstable unsaturated,[10] rather than benzenoid, products are formed.

The availability of an alternative site for nucleophilic attack in 3-chlorotropone (IIb) was demonstrated by the effect of dimethylamine. In solution in acetonitrile reaction was rapid even at 0°, giving approximately equal amounts of 2- and 3-dimethylaminotropones. Under the same conditions, 2-chlorotropone was quantitatively converted into the 2-dimethylamino-compound. The susceptibility of the 2-position of 3-chlorotropone to nucleophilic attack contrasts with the behaviour of 2,3-dichlorotropone, in which the 3-substi-

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* The recent statement [4] that 3- and 4-chlorotropones can be prepared by this means appears to have been erroneously based, and these compounds are hitherto undescribed.

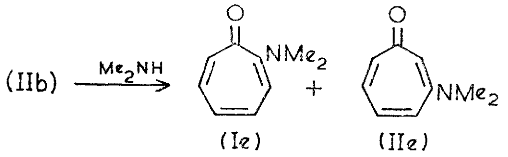
[7] S. Seto, H. Sugiyama, and H. Toda, *Chem. Comm.*, 1968, 562.

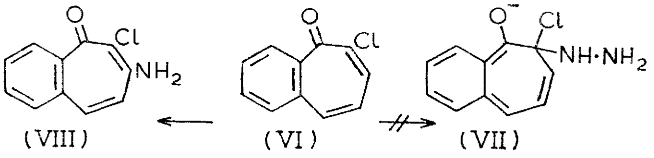
[8] T. Nozoe, T. Mukai, and J. Minegishi, *Proc. Japan Acad.*, 1952, **28**, 287.

[9] E. J. Forbes, D. C. Warrell, and W. J. Fry, *J. Chem. Soc.* (*C*), 1967, 1693.

[10] K. Kikuchi, *Bull. Chem. Soc. Japan*, 1967, **40**, 355.

tuent is preferentially hydrolysed.[11] Examples of *cine*-substitution have been previously observed in reactions involving derivatives of tropolone,[12] and in the case of protic nucleophiles, are most acceptably rationalised in terms of an addition–elimination mechanism.





An interesting comparison is provided by the behaviour of 7-chloro-2,3-benzotropone, encountered during unsuccessful attempts to prepare the corresponding azide. The halogen atom of this compound (VI) was extremely resistant to direct displacement, doubtless owing to the instability of the intermediate anion (VII), in which effective delocalisation of charge can occur only at the cost of disruption of aromaticity. No reaction resulted from prolonged treatment with sodium azide in hot dimethylformamide or dimethyl sulphoxide; the only effective reagent was anhydrous hydrazine, which, however, afforded an amino-derivative without displacement of chloride. No information assisting the location of the amino-group in this compound was obtained from the n.m.r. spectrum, but i.r. data allowed a tentative decision in favour of (VIII). The established relationship between the symmetric and antisymmetric stretching vibrations of primary amines [13,14] appears to hold quite well for the 3- and 4-aminotropones (see Table 1), but breaks down for the 2-isomer, as expected for an amino-group involved in intramolecular hydrogen bonding.[14] The lesser, but nevertheless significant, deviation observed in the data for (VIII) is attributable to the presence of NH • • • Cl hydrogen bonding, which is perhaps more than usually substantial in this compound owing to the acidifying effects of conjugation on the amino-group.

TABLE 1

NH_2 Stretching frequencies of primary aminotropones (cm.$^{-1}$) [a]

Amine	ν_{as}	ν_s (obs.)	ν_s (calc.)	ν_s (calc.) — ν_s (obs.)
(Id)	3503	3360	3412	52
(IId)	3506	3410	3414	4
(IIId)	3505	3410	3413	3
(VIII)	3503	3385	3412	27

[a] Frequencies ±2 cm.$^{-1}$, determined for solutions in CH_2Cl_2, unchanged on dilution. [b] Calc. from ν_{as}, using the empirical relation:[14] $\nu_s = 1023 + 0{\cdot}682\nu_{as}$.

Mass Spectra.—The principal fragment ions observed in the mass spectra of the 3- and 4-substituted tropones described are shown in Table 2.

TABLE 2

Mass spectra of 3- and 4-substituted tropones

	Major peaks [m/e (% rel. abundance)]
(IIc)	147 (M^+, 40), 119 (3), 91 (95), 65 (20), 64 (100), 63 (60), 52 (23), 51 (30), and 50 (25); m^*, 45·0 ($91 \longrightarrow 64$).
(IIIc)	147 (M^+, 40), 119 (40), 93 (60), 91 (95), 65 (60), 64 (100), 63 (50), 52 (33), 51 (20), and 50 (20).
(IIb)	142, 140 (M^+, 1:3, 46); 114, 112 (1:3, 100), 77 (79), 61 (55), 60 (45), 51 (55), and 50 (45); m^* 53·0 ($112 \longrightarrow 77$) and 33·8 ($77 \longrightarrow 51$).
(IIIb)	142, 140 (M^+, 1:3, 46), 114, 112 (1:3, 100), 77 (63), 51 (36), and 50 (27); m^* 52·9 ($112 \longrightarrow 77$).
(IId)	121 (M^+, 4), 93 (100), 66 (33), 65 (17), 52 (7), 51 (10), and 50 (9); m^* 46·9 ($93 \longrightarrow 66$).
(IIId)	121 (M^+, 20), 93 (100), 66 (52), 65 (32), 52 (20), 51 (14), and 50 (9); m^* 46·9 ($93 \longrightarrow 66$).
(IIe)	149 (M^+, 10), 122 (8), 121 (80), 120 (100), 105 (13), 91 (6), 77 (24), and 51 (24).

In the spectra of the azides (IIc) and (IIIc) stepwise loss of N_2, CO, HCN, and H_2CN is indicated; the spectra differ from that of the 2-isomer only in the relatively high intensity of the peak at *m*/*e* 119 in the latter, due presumably to stabilisation of $[M - N_2]^+$ *via* ring fission.[1] The fragmentation patterns of 3- and 4-chlorotropones are similar to that of 2-isomer,[15] and feature the initial expulsion of CO characteristic of tropones, with the rest of the spectrum being due to chlorobenzene.[16]

The parent ion in the spectra of 3- and 4-aminotropones (IId) and (IIId) is rather weak, in contrast to that shown by 2-aminotropone (Id),[15] where it is the base peak. In this, the aminotropones are apparently analogous to the three tropolones, where the relative prominence of the molecular ion in the spectrum of the 2-isomer (Ia) has been associated with the ability of the two oxygen atoms in this compound to share the positive charge by transference of the hydrogen atom between them.[15] However a strong M^+ peak is also present in the spectrum of 2-dimethylaminotropone (Ie),[15] whereas in that of the 3-isomer (IIe) (Table 2) it is again weak, suggesting that the important factor is more probably the more effective delocalisation available for the odd electron in 2-substituted tropones.

EXPERIMENTAL

Spectra were measured with Perkin-Elmer model 125, Unicam SP 800, and Varian A-60 instruments; unless otherwise specified, u.v. spectra are of solutions in ethanol, and n.m.r. spectra of solutions in deuteriochloroform, with

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[11] S. Seto, *Sci. Reports Res. Inst., Tôhoku Univ.*, 1953, **37**, 275, 297.

[12] T. Nozoe and Y. Kitahara, *Proc. Japan Acad.*, 1954, **30**, 204; K. Doi, *Bull. Chem. Soc. Japan*, 1960, **33**, 887; 1961, **34**, 497; T. Toda, *ibid.*, 1967, **40**, 588, and references therein.

[13] L. J. Bellamy and R. L. Williams, *Spectrochim. Acta*, 1957, **9**, 341; J. E. Stewart, *J. Chem. Phys.*, 1959, **30**, 1259.

[14] P. J. Krueger and H. W. Thompson, *Proc. Roy. Soc., A*, 1959, **250**, 22.

[15] J. M. Wilson, M. Ohashi, H. Budzikiewiez, C. Djerassi, Sho Ito, and T. Nozoe, *Tetrahedron*, 1963, **19**, 2247; H. Budzikiewiez, C. Djerassi, and D. H. Williams, ' Interpretation of Mass Spectra of Organic Compounds,' Holden-Day, San Francisco, **1964**, p. 213.

[16] F. W. McLafferty, *Analyt. Chem.*, 1962, **34**, 16.

tetramethylsilane as internal reference. Mass spectra were obtained with an A.E.I. MS-9 instrument, operating at an ionising potential of 70 ev, by direct insertion (source temperature 200°).

3-Hydroxytropone, m.p. 184—186° (decomp.) (lit.,[6a] 183°) was prepared from 3,5-dimethoxybenzoic acid rather than gallic acid.[6a] The toluene-*p*-sulphonate, obtained by reaction with toluene-*p*-sulphonyl chloride in pyridine, crystallised from benzene in colourless rhombs, m.p. 98° (lit.,[7] 92°). Reaction of this compound with excess of sodium azide in dimethyl sulphoxide for 5 hr. at 40°, followed by chromatography of the crude product on alumina (ether–cyclohexane 2 : 1) gave only toluene-*p*-sulphonamide, m.p. 135—137°. None of the fractions showed azide i.r. bands.

Reaction of the Sodium Salt of 3-*Hydroxytropone with Oxalyl Chloride*.—3-Hydroxytropone (390 mg.) in water (3 ml.) was neutralised with 2N-sodium hydroxide, the solution was evaporated to dryness, and the residue was heated at 120°/10 mm. for 2 hr. The salt was treated at 0° with a solution of oxalyl chloride (1·6 ml.) in dry benzene (4 ml.) and the mixture was stirred at 20° for 12 hr. The filtered solution was evaporated *in vacuo*, giving a mobile brown oil, $\lambda_{max.}$ (ether) 233 and 283 mμ ($E_{1\,cm.}^{1\%}$ 540 and 230), $\nu_{max.}$ (film) 1605 and 1020 cm.$^{-1}$, τ 3·6—4·2 (complex m) only, *m/e* 163, 161, 159 (intensity ratio 1 : 6 : 9); 142, 140 (1 : 3); 114, 112 (1 : 3); and 77, 51, 50; *m** 53·0 ($112 \longrightarrow 77$).

In the atmosphere, this product absorbed moisture and crystallised; trituration with anhydrous ether afforded colourless needles, m.p. 102—105° (sealed tube), which rapidly absorbed moisture and reliquefied on further exposure. Short path distillation of the resulting oil on to a cold finger at 75° (oil bath)/25 mm. gave crystals, m.p. 15—18°, of 3-*chlorotropone hemihydrate*, $\lambda_{max.}$ 235, 240, 248, 305, and 316 mμ (ε 22,000, 24,900, 16,100, 4700, and 4200) $\nu_{max.}$ (CH_2Cl_2) 1635, 1590, and 1525 cm.$^{-1}$ (Found: C, 56·4; H, 4·1. $C_7H_5ClO,0{\cdot}5H_2O$ requires C, 56·2; H, 4·0%), τ 2·7—3·3 (complex).

Direct treatment of the oily initial product with water, followed by isolation with dichloromethane resulted in almost quantitative conversion into hydrated 3-chlorotropone, sufficiently pure for most purposes, though it darkened and resinified on storage at room temperature.

A solution of 3-chlorotropone (100 mg.) in dry benzene (5 ml.) when treated with oxalyl chloride (0·5 ml.) effervesced vigorously and gave, after removal of the solvent and excess of acid chloride *in vacuo*, a brown oil with spectroscopic properties identical with those described for the oily precursor of 3-chlorotropone. Decomposition with water again resulted in almost quantitative conversion into 3-chlorotropone.

4-*Chlorotropone*.—4-Hydroxytropone (prepared by the method of Meinwald and Chapman [6b]) (480 mg.) was converted into its sodium salt and treated with oxalyl chloride as described for the 3-isomer. The oily product obtained by evaporation of the solvent showed $\nu_{max.}$ (film) 1616 and 1015 cm.$^{-1}$, $\lambda_{max.}$ (in cyclohexane) 231 and 286 mμ ($E_{1\,cm.}^{1\%}$ 485 and 235), τ 4·0—4·4 (complex m) *m/e* 163, 161, 159 (1 : 6 : 9); 142, 140 (1 : 3); 114, 112 (1 : 3), and 77, 51, 50. This product was hygroscopic, and solidified on absorption of atmospheric moisture.

Addition of water, followed by isolation with dichloromethane, crystallisation of the crude product from acetone at −20°, and sublimation at 100°/30 mm. afforded colourless needles, m.p. 104°, of 4-*chlorotropone* (Found: C, 59·9; H, 3·7; Cl, 25·1. C_7H_5ClO requires C, 59·8; H, 3·6; Cl, 25·2%), $\lambda_{max.}$ 231, 307, and 316 mμ (ε 23,300, 8800, and 8700), $\nu_{max.}$ (CH_2Cl_2) 1634, 1585, and 1514 cm.$^{-1}$, τ 2·8—3·3 (unresolved m). This compound also reacted vigorously when treated with oxalyl chloride in benzene at 20°, regenerating the hygroscopic oil with spectroscopic properties identical with those already described.

Hydrolysis of 3- *and* 4-*Chlorotropones*.—A solution of the 3-chloro-compound (50 mg.) in ethanol (1 ml.) and 4N-hydrochloric acid (1 ml.) was heated on a steam-bath for 1 hr. More acid (1 ml.) was added, and the mixture was heated under reflux for 9 hr. Evaporation *in vacuo* and trituration of the residue with dichloromethane afforded 3-hydroxytropone hydrochloride (45 mg.); recrystallisation from water gave 3-hydroxytropone, m.p. 184—186° (decomp.).

4-Chlorotropone was hydrolysed under similar conditions to 4-hydroxytropone (70% yield), m.p. 212° (lit.,[6b] 209—211°).

Addition of 2N-sodium hydroxide (2 ml.) to a solution of 3- or 4-chlorotropone (100 mg.) in ethanol (2 ml.) resulted in rapid darkening and eventual deposition of amorphous brown material; no recognisable products were isolated.

3- *and* 4-*Azidotropones*.—Sodium azide (1·1 g.) suspended in a solution of the appropriate chlorotropone (0·5 g.) in dimethyl sulphoxide (3 ml.) was stirred under nitrogen for 18 hr. at 30°. After dilution with ice–water the product was isolated with dichloromethane; the crude azide was taken up in a little warm light petroleum (b.p. 40—60°) which, when cooled, deposited straw-coloured needles (90%) of 3-*azidotropone*, m.p. 61—63°, $\lambda_{max.}$ (cyclohexane) 226, 273, 299, 312, and 327 mμ (ε 21,500, 15,400, 2900, 2500, and 1600), $\nu_{max.}$ (Nujol) 2120 (antisymm. N_3), 1265, and 1240 (symm. N_3) cm.$^{-1}$; $\nu_{max.}$ (CH_2Cl_2) 2120, 1642, 1585, 1557, and 1538 cm.$^{-1}$, τ 2·7—3·5 (unresolved m) (Found: C 57·0; H, 3·4; N, 28·7. $C_7H_5N_3O$ requires C, 57·1; H, 3·5; N, 28·6%).

4-*Azidotropone* (80%) crystallised from light petroleum (b.p. 40—45°) at −20°; m.p. 38—39°, $\lambda_{max.}$ (cyclohexane) 230, 243, 252, 261, 272, 310, and 325 mμ (ε 22,400, 19,200, 19,100, 18,300, 14,500, 16,700, and 16,700), $\nu_{max.}$ (CH_2Cl_2) 2115, 1640, 1606, 1583, and 1518 cm.$^{-1}$, $\nu_{max.}$ (Nujol) 2110 (asymm. N_3), 1280, and 1230 (symm. N_3) cm.$^{-1}$, τ 3·0—3·6 (unresolved m) (Found: C, 57·4; H, 3·5; N, 28·9%).

Reduction of 3- *and* 4-*Azidotropones*.—A solution of the azide (50 mg.) in ethanol (5 ml.) was hydrogenated over 10% palladium–charcoal, giving a quantitative yield of the crude amine. 3-Aminotropone sublimed at 120°/0·01 mm., giving yellow crystals, m.p. 192—194° (decomp.) (lit.,[7] 188°) (Found: C, 69·4; H, 5·9; N, 11·6%. Calc. for C_7H_7NO: C, 69·4; H, 5·8; N, 11·6%), $\lambda_{max.}$ 263, 275, 303, and 313 mμ (ε 22,700, 20,500, 5300, and 4900) $\nu_{max.}$ (CH_2Cl_2) 3506, 3410, 1644, 1625, 1592, and 1560 cm.$^{-1}$.

4-Aminotropone crystallised from methanol at −20° as yellow needles, m.p. 214° (decomp.; sealed tube) [lit.,[17] 218° (decomp.)] (Found: C, 69·4; H, 5·7%), $\lambda_{max.}$ 227, 260, and 362 mμ (ε 17,000, 5700, and 20,000), $\nu_{max.}$ 3505, 3410, 1644, 1620, 1602, and 1555 cm.$^{-1}$.

Each aminotropone was hydrolysed by heating for 4 hr. with excess of 4N-sodium hydroxide on a steam-bath; acidification to pH 3 followed by continuous ether extraction afforded the corresponding hydroxytropone.

Reaction of 3-*Chlorotropone with Dimethylamine*.—A solution of 3-chlorotropone (60 mg.) and dimethylamine (1 ml.)

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[17] K. Doi, *Bull. Chem. Soc. Japan*, 1960, **33**, 887.

in acetonitrile (4 ml.) was kept at 0°; t.l.c. indicated that the reaction was complete in 30 min. Aqueous sodium carbonate was added and the solution was extracted with ether, giving a yellow oil (30 mg.), shown to be 2-dimethylaminotropone [18] by comparison of its spectra with those of an authentic sample prepared by reaction of 2-chlorotropone with dimethylamine in acetonitrile, and also by comparison of the picrates, m.p. 150—151° (lit.,[18] 155°). Further basification of the aqueous mother liquors with 4N-sodium hydroxide was followed by thorough extraction with dichloromethane, giving, after evaporation, oily yellow crystals (34 mg.). Dry column chromatography on alumina (Woelm; activity III) in 2% methanol–ether, followed by crystallisation from methanol–ether at −20°, gave 3-*dimethylaminotropone*, m.p. 159—161° (decomp.) (Found: C, 72·7; H, 7·4; N, 9·2. $C_9H_{11}NO$ requires C, 72·5; H, 7·4; N, 9·4%), $\lambda_{max.}$ 277, 283, 310, and 324 mμ (ε 23,000, 23,000, 11,000, and 9200), $\nu_{max.}$ (CH_2Cl_2) 1644, 1587, and 1540 cm.$^{-1}$. The *picrate* had m.p. 173—175° (decomp.) (from methanol) (Found: C, 47·9; H, 3·6. $C_{15}H_{14}N_4O_8$ requires C, 47·6; H, 3·7%).

Decomposition of 3- *and* 4-*Azidotropones*.—(*a*) 3-*Azidotropone*. The azide (100 mg.) in *o*-dichlorobenzene (2 ml.) was heated to 160°; evolution of nitrogen became vigorous above 140°, and the mixture darkened and deposited polymeric material. After 10 min., the cooled solution was diluted with light petroleum (b.p. 40—60°), and the polymeric solid was collected and washed with light petroleum. The residue was extracted with ethanol, and the extract was filtered and evaporated.

T.l.c. revealed 3-aminotropone as the only mobile constituent of the crude oily product; this compound (58% yield) was isolated by dry column chromatography on alumina in 5% methanol–ether. Similar results were obtained when aniline was used as the thermolysis medium.

A 0·5% ethereal solution of 3-azidotropone (20 ml.) cooled to 10° under nitrogen was irradiated in a Pyrex tube 10 cm. from a 500 w medium-pressure mercury lamp. After 4 hr. the azide absorption at 2120 cm.$^{-1}$ had disappeared, but only intractable polymeric solid was produced.

(*b*) 4-*Azidotropone*. This also decomposed rapidly when heated above 140° in *o*-dichlorobenzene; a dark polymeric material was again formed, from which a small quantity (*ca*. 5%) of 4-aminotropone was isolated by extraction with hot ethanol. The results of photolysis experiments were similar.

6-*Amino*-7-*chloro*-2,3-*benzotropone* (VIII).—A solution of 7-chloro-2,3-benzotropone [19] (200 mg.) and anhydrous hydrazine (0·5 ml.) in anhydrous tetrahydrofuran (10 ml.) under nitrogen was kept at 35° for 9 hr. Dilution with water and isolation with ether gave 6-*amino*-7-*chloro*-2,3-*benzotropone*; sublimation at 120°/10 mm. and recrystallisation from benzene gave yellow needles, m.p. 170—171°, $\lambda_{max.}$ (EtOH) 248, 293, 375, and 416 mμ (ε 24,400, 16,100, 12,200, and 6000), $\nu_{max.}$ (CH_2Cl_2) 3503, 3385, 1610, 1588, 1580, 1543, and 1514 cm.$^{-1}$ (Found: C, 64·3; H, 3·6; N, 6·5; Cl, 17·4. $C_{11}H_8ClNO$ requires C, 64·2; H, 3·6; N, 6·8; Cl; 17·2%), *m*/*e* 207 and 205 (1 : 3, M^+).

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