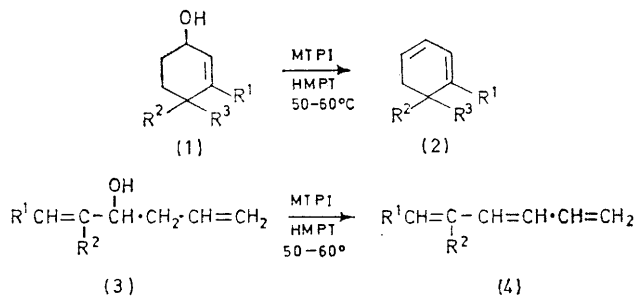


Generation of Acyclic Trienes and Cyclic Dienes by Mild Dehydration and Dehydrohalogenation in Aprotic Media

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Substituted hexa-1,3,5-trienes and cyclohexa-1,3-dienes can be generated under mild conditions in hexamethylphosphoric triamide (HMPT), by dehydration of an appropriately substituted hexadienol or cyclohexenol or by dehydrohalogenation of dienyl or cyclohexenyl bromides, by the action of lithium iodide or methyltriphenoxyphosphonium iodide (MTPI) in HMPT. The MTPI reaction products can be rationalized on the basis of simple E_2 -type dehydrohalogenation of intermediary allylic halides; however, the intermediates in the lithium iodide dehydrohalogenations appear to have a greater degree of carbocation character, and to be similar to dehydrohalogenations with silver nitrate in dimethyl sulphoxide.

RECENTLY we reported¹ that substituted hexa-1,3,5-trienes (4) and cyclohexa-1,3-dienes (2) could be prepared



$R^1 = H$ or Me, $R^2 = H$, Me, or Et

in good yield by direct dehydration of appropriately substituted hexadienols (3) or cyclohexenols (1) with methyltriphenoxyphosphonium iodide (MTPI) in hexa-

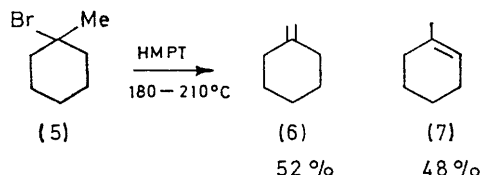
methylphosphoric triamide (HMPT) under mild conditions. Monson² had previously shown that HMPT could be utilized to dehydrate saturated alcohols directly by heating in solution in the pure solvent until the olefinic product and dimethylamine codistilled from the mixture, usually after a reaction temperature of 200 °C had been achieved. Monson also observed³ dehydrohalogenation of primary alkyl halides in HMPT at 180–210 °C, obtaining unrearranged alk-1-enes in good yield. However 1-bromo-1-methylcyclohexane (5) yielded both methylenecyclohexane (6) and 1-methylcyclohexene (7) in approximately equal proportions. It was suggested that the high reaction temperature was responsible for olefin rearrangement. Hutchins and

¹ C. W. Spangler and T. W. Hartford, *Synthesis*, 1976, 108.

² R. S. Monson, *Tetrahedron Letters*, 1971, 567.

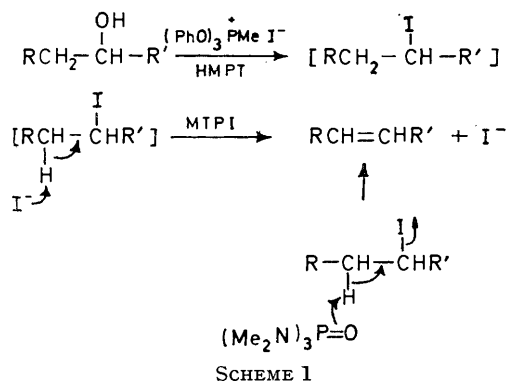
³ R. S. Monson, *Chem. Comm.*, 1971, 113.

his co-workers⁴ demonstrated that secondary alcohols could be dehydrated under much milder conditions in HMPT by methyltriphenoxyphosphonium iodide, a reagent previously utilized for conversion of alcohols into

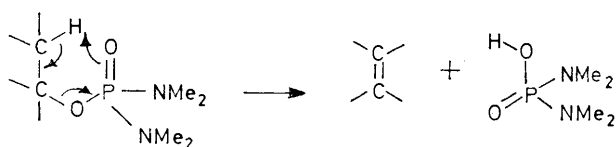
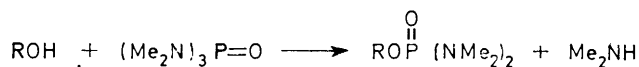


the corresponding iodides.^{5,6} Presumably the mechanism involves initial conversion of the alcohol into the iodide with inversion, followed by dehydrohalogenation by either iodide ion or HMPT. Partial evidence for this interpretation is an increased rate of dehydrohalogenation when 2-iodo-octane in HMPT is treated with MTPI. Saytzeff elimination dominates olefin formation in all cases. These authors also noted that tertiary alcohols were almost totally inert to dehydration under these conditions.

We have found that MTPI in HMPT is a highly effective system for dehydration of both substituted hexadienols and cyclohexenols, producing conjugated hexa-1,3,5-trienes and cyclohexa-1,3-dienes, respectively.¹



The mechanism for this process proposed by Hutchins *et al.*⁴ (Scheme 1) prompted us to investigate these



SCHEME 2

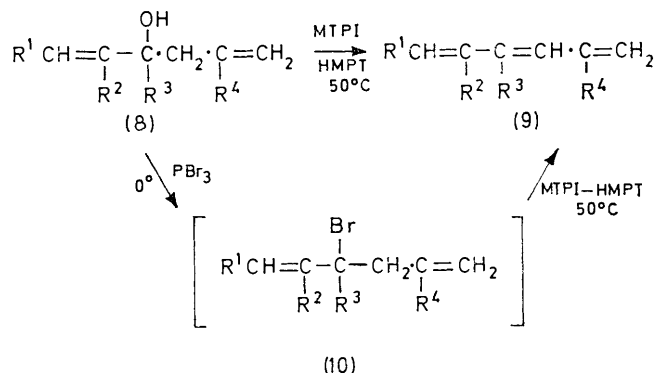
conversions in greater detail. Monson and Priest⁷ suggested that E_i pathways may dominate in the

⁴ R. O. Hutchins, M. G. Hutchins, and C. A. Milewski, *J. Org. Chem.*, 1972, **37**, 4190.

⁵ S. R. Landaner and H. N. Rydon, *J. Chem. Soc.*, 1954, 2224.

absence of MTPI (Scheme 2) and that carbocation processes were not operative. However, dimethylamine formation is not observed in the MTPI process. In both Schemes it appears that carbocation processes are unimportant.

It seemed that if alkyl iodides were intermediates in the MTPI reactions, then the more readily prepared bromides should yield equivalent results. Therefore we compared product distributions in the direct dehydration of several substituted hexadienols (8) by MTPI-HMPT with those in the dehydrohalogenation of the equivalent bromides (10) by MTPI in HMPT. The



- a; $R^1 = R^2 = R^3 = R^4 = \text{H}$
 b; $R^1 = \text{Me}, R^2 = R^3 = R^4 = \text{H}$
 c; $R^1 = R^3 = R^4 = \text{H}, R^2 = \text{Me}$
 d; $R^1 = R^2 = R^4 = \text{H}, R^3 = \text{Me}$
 e; $R^1 = R^2 = R^3 = \text{H}, R^4 = \text{Me}$

dienyl bromides were also dehydrohalogenated with lithium iodide in HMPT under identical conditions, and the product ratios were compared with the MTPI results. In order to evaluate the possible contribution of carbocation processes in the product-generating step, the bromides were also treated with silver nitrate in dimethyl sulphoxide, and these product distributions were compared with the others. The results are summarized in the Table.

In comparing the trienic products from the reaction of either the dienol or the dienyl bromide, the similarity of the distributions confirms Hutchins'⁴ proposal that the dehydration process proceeds through the halide (iodide). Thus (8b) and (10b) yield identical products, both in composition (68% hepta-1,3,5-triene and 32% hepta-1,3,6-triene) and in ratio of geometric isomers. A separate experiment showed that these isomer ratios are not affected by equilibration with excess of MTPI. Tertiary dienols can be dehydrated by this procedure, whereas saturated tertiary alcohols are inert.

Lithium iodide in HMPT does not dehydrate the dienols employed in this study; however, it can dehydrohalogenate the intermediary dienyl bromides, producing product distributions different from the





⁶ J. Verheyden and J. Moffat, *J. Org. Chem.*, 1970, **35**, 2319.

⁷ R. S. Monson and D. N. Priest, *J. Org. Chem.*, 1971, **36**, 3826.

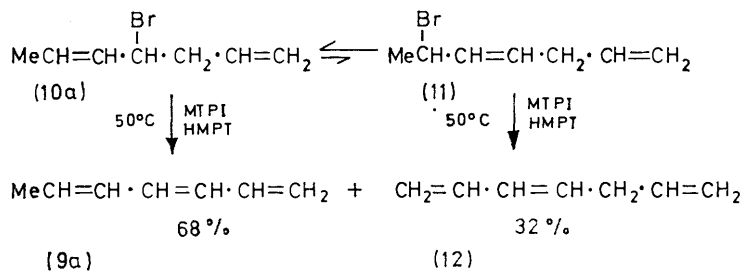
MTPI results, as a result of varying degrees of ion pairing in the two reagents. In fact, the lithium iodide dehydrohalogenation product distributions are more similar to the silver nitrate-dimethyl sulphoxide results, which indicates that there is more carbocation character in the lithium iodide process than in the MTPI reactions, the latter being more closely related to an E_2 -type transition state as originally proposed.⁴ It has previously been shown that dienyl bromides such

Dehydration of 3-methylcyclohex-2-enol (15) however yields a mixture of 1-methylcyclohexa-1,3-diene (19), 2-methylcyclohexa-1,3-diene (20), and 3-methylenecyclohexa-1,3-diene (21). If we assume that a process similar to that described for the acyclic trienes is operative, then conversion of the alcohol into a mixture of allylic halides, followed by dehydrohalogenation readily accounts for the observed product distribution. However, a carbocation process could also be envisaged,

Dehydration and dehydrohalogenation product distributions in the methylhexa-1,3,5-triene system

Reaction ^{a,b}	Yield %	% of total product							
		1-Me triene	2-Me triene	3-Me triene	Unconj. Me triene				
(8b), MTPI-HMPT	95	68 ^c			32 ^k	Tr			
(8c), MTPI-HMPT	53		100 ^d					Tr	
(8d), MTPI-HMPT	16			58 ^e	20 ^l		22		
(8e), MTPI-HMPT	56		11 ^d					89	
(10b), MTPI-HMPT	50	68 ^f			32 ^k	Tr			
(10b), LiI-HMPT	56	89 ^g			11 ^k				
(10b), AgNO ₃ -Me ₂ SO	46	81 ^h			19 ^k	Tr			
(10c), MTPI-HMPT	40		100 ^d					Tr	
(10d), LiI-HMPT	50			75 ⁱ	17 ^l		8		
(10d), AgNO ₃ -Me ₂ SO	30			58 ^j	40 ^l		2		
(10d), HMPT, 190 °C	20			10 ^d	27 ^l		29		
(10e), LiI-HMPT	11		11 ^d					74	15
(10e), AgNO ₃ -Me ₂ SO	11		11 ^d					83	6

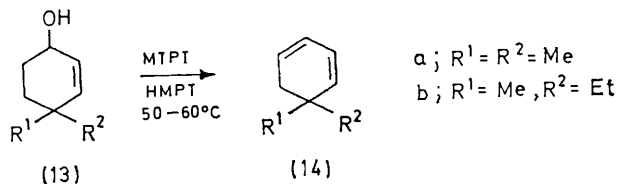
^a All reactions carried out at 50–60 °C (H₂O bath) unless otherwise specified. ^b For (8a), HMPT-MTPI, 56% yield of (9a) (69% *E*, 31% *Z*); for (8b), LiI-HMPT, 15% (9a) (69% *E*, 31% *Z*); for (8b), AgNO₃-Me₂SO, 14% product (56% *E*, 18% *Z*, 26% cyclohexa-1,3-diene). ^c 67% *E,E* and 33% *Z,E*. ^d 100% *E*. ^e 64% *E*, 36% *Z*. ^f 67% *E,E*, 33% *Z,E*. ^g 62% *E,E*, 38% *Z,E*. ^h 72% *E,E*, 28% *Z,E*. ⁱ 77% *E*, 23% *Z*. ^j 74% *E*, 26% *Z*. ^k (*E*)-Hepta-1,3,6-triene. ^l 3-Methylenehexa-1,5-diene. Tr = Trace (<0.5%).



SCHEME 3

as (10b) exist as a mixture of allylic isomers,^{8,9} and thus the dehydrohalogenations by MTPI can be visualized as two separate E_2 eliminations (Scheme 3).

Dehydration of substituted cyclohex-2-enols with MTPI in HMPT may be interpreted in a similar fashion.



Both 4,4-dimethylcyclohex-2-enol (13a) and 4-ethyl-4-methylcyclohex-2-enol (13b) yield the corresponding 5,5-dialkylcyclohexa-1,3-diene (14) in high yield (60–70%).¹

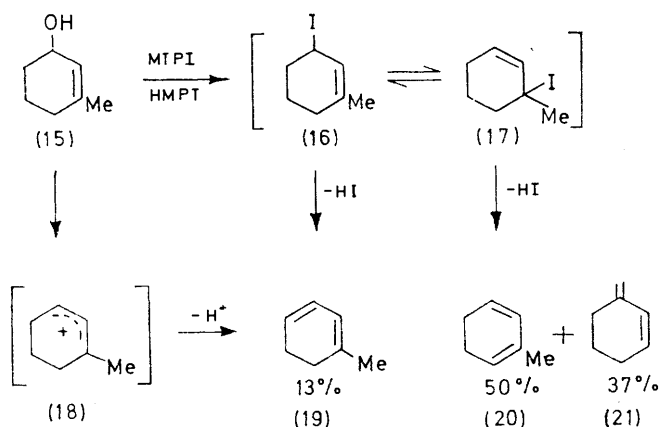
⁸ J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *J. Amer. Chem. Soc.*, 1960, **82**, 2537.

leading to identical results (Scheme 4). Similar reactions proceeding through (18) have been studied previously,¹⁰ and the product distributions are similar, but not identical (Scheme 5). However, the obviously different reaction conditions (50 vs. 250 °C; HMPT vs. gas phase) could easily account for these discrepancies.

A more dramatic demonstration that carbocations may intervene in MTPI reactions is found in the differing product distributions in the dehydrations of 2-methylhexa-1,5-dien-3-ol (8c) and 2-methylhexa-1,5-dien-4-ol (8e), the former yielding *only* 2-methylhexa-1,3,5-triene (9c), in 53% yield,¹ and the latter primarily 1-methylcyclohexa-1,3-diene (Scheme 6). One can envisage this latter process as a cyclization of an intermediary

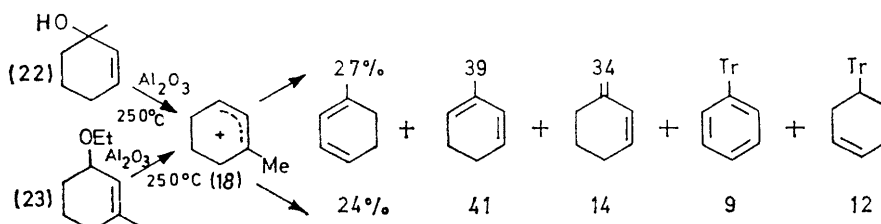
⁹ C. W. Spangler and G. F. Woods, *J. Org. Chem.*, 1963, **28**, 2245; 1965, **30**, 2218.

¹⁰ C. W. Spangler and R. P. Hennis, *J. Org. Chem.*, 1971, **36**, 917.

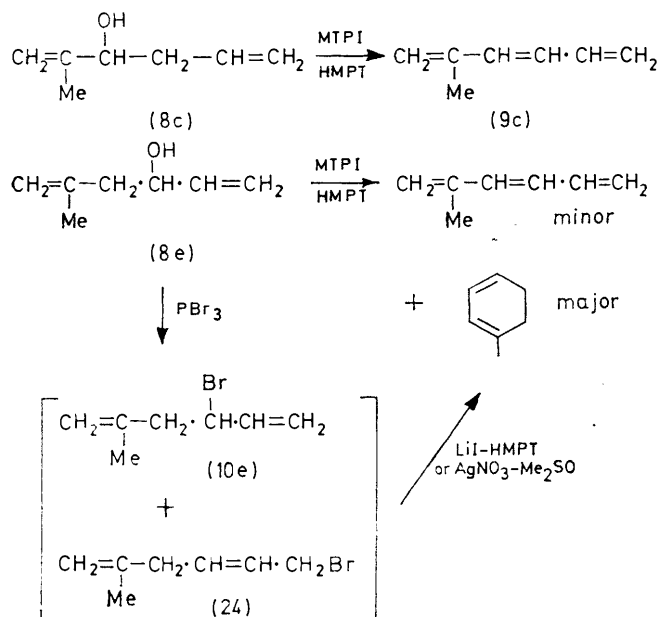


SCHEME 4

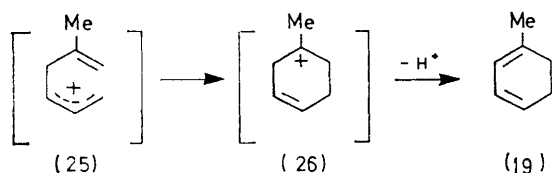
carbonium ion followed by proton loss (Scheme 7). The striking difference in the reaction paths followed by the



SCHEME 5



SCHEME 6



SCHEME 7

two isomeric methylhexadienols underlines the care with which syntheses need to be planned when MTPI-HMPT is used as a dehydration reagent. However, in those cases where the direction of dehydration may be controlled, the MTPI-HMPT procedure is a superior method of generating acyclic conjugated 1,3,5-trienes and cyclic conjugated 1,3-dienes, in both yield and ease of isolation.

EXPERIMENTAL

G.l.c. was performed with an Aerograph 202-1B dual column instrument equipped with a Hewlett-Packard 3370A electronic integrator for peak area measurement, and 20 ft 15% 1,2,3-tris-2-cyanoethoxypropane (TCEP) SS columns (column temperature 75 °C; He pressure 60 lb in⁻², 60 ml min⁻¹ flow rate). U.v. spectra were recorded with a Perkin-Elmer 202 and i.r. spectra with an IR-8 spectrophotometer. N.m.r. spectra were determined for solutions in CDCl₃ (Me₄Si standard) with a Varian A-60A spectro-

meter. All triene spectra were recorded for mixtures of geometric isomers unless otherwise stated.

Dehydration of Dienols. General Procedure.—The dienol (0.050 mol) was added to a mixture of MTPI (35 g) in HMPT (100 ml). The mixture rapidly darkened, and was placed in a water-bath (50–55 °C) and stirred for 2 h. It was then distilled at 50 °C and 10–15 mmHg and the product was trapped in a solid CO₂-acetone bath. The products were warmed to room temperature and analysed immediately by g.l.c.

Dehydrohalogenation of Dienyl Bromides. General Procedure.—The dienyl bromide (0.10 mol) was dissolved in HMPT (200 ml) and either MTPI (70 g) or lithium iodide (27 g) was added all at once, with stirring. The reaction was exothermic and the temperature rose rapidly to 50–60 °C as the mixture darkened. After the reaction had subsided the mixture was stirred at 50–55 °C (water-bath) for 1 h, then distilled, and the product was isolated and analysed as above.

Dehydrohalogenation of Dienyl Bromides by Silver Nitrate in Dimethyl Sulphoxide.—The dienyl bromide (0.20 mol) dissolved in dimethyl sulphoxide (50 ml) was added dropwise to a solution of silver nitrate (41 g) in dimethyl sulphoxide (100 ml) in the dark. Immediate precipitation of silver bromide took place exothermically. The mixture was then stirred at 50–55 °C (water-bath) for 1 h, and distilled, and the product was isolated and analysed as above.

Attempted Dehydrohalogenation of 3-Bromo-3-methylhexa-1,5-diene in HMPT.—The diene (35 g, 0.20 mol) was dissolved in HMPT (130 ml) (no evidence of reaction was observed) and stirred at 25 °C for 1 h. The temperature was then raised slowly to 200 °C. No product distilled over

until the pot temperature had reached 190 °C, and a distillate was then obtained smelling strongly of dimethylamine. After distillation ceased, the product was washed with water and filtered through anhydrous magnesium sulphate. The product (3.6 g) was then analysed immediately by g.l.c.

Attempted Equilibration of Hepta-1,3,5-triene with MTPI in HMPT.—Hepta-1,3,5-triene (5 g) [a mixture of 5-methylcyclohexa-1,3-diene (10.1%), (*E,E*)-hepta-1,3,5-triene (51.1%), and (*Z,E*)-hepta-1,3,5-triene (38.8%)] was dissolved in HMPT (100 ml). MTPI (35 g) was added and the mixture kept at 50 °C (water-bath) for 2 h. It was then distilled and the product isolated as above and analysed by g.l.c. (yield 4.0 g; 80% recovery). 5-Methylcyclohexa-1,3-diene (14.8%), (*E,E*)-hepta-1,3,5-triene (52.1%), and (*Z,E*)-hepta-1,3,5-triene (33.1%) were present. No new products were formed.

Attempted Dehydration of Hepta-1,5-dien-4-ol with Lithium Iodide in HMPT.—Hepta-1,5-dien-4-ol (11.2 g, 0.10 mol) was dissolved in HMPT (200 ml), followed by lithium iodide (35 g). The mixture darkened and became viscous, and was stirred at 50–55 °C (water-bath) for 2 h, after which distillation at reduced pressure was attempted. Only traces of low-boiling material were obtained. There was no evidence of hepta-1,3,5-triene.

Identification of Products.—Hepta-1,3,5-triene and 3-

methylhexa-1,3,5-triene were prepared separately as previously described⁹ and the geometric identity of the isomers was established by comparison with authentic samples, also previously described.^{9,11} The preparation and identification of 2-methylhexa-1,3,5-triene and comparison with authentic samples have also been recently described.¹ Hepta-1,3,6-triene was compared with a commercial sample (Chemical Samples Co., Columbus, Ohio). The isolation and identification of 1-, 2-, and 5-methylcyclohexa-1,3-diene and 3-methylenecyclohexene have been described previously.¹² As an example of the techniques utilized in this study, 2-methylhexa-1,3,5-triene was identified as follows. The crude product from the MTPI–HMPT dehydration of (8c) was subjected to g.l.c. purification and the main peak in the chromatogram was isolated by trapping the effluent in a V-tube immersed in a solid CO₂–acetone bath and submitted to i.r., u.v., and n.m.r. analysis: τ (CDCl₃) 8.25 (3 H, s), 5.30 (4 H, s), and 4.05 (3 H, s); λ_{max} (EtOH) 267 (ϵ 35 000), 257 (44 400), and 248 nm (34 400); ν_{max} (film) 3 050, 2 925, 1 780, 1 600, 1 440, 1 360, 1 300, 1 160, 1 100, 945, and 887 cm⁻¹.

[6/365 Received, 23rd February, 1976]

¹¹ C. W. Spangler, T. P. Jondahl, and B. Spangler, *J. Org. Chem.*, 1973, **38**, 2478.

¹² C. W. Spangler and N. Johnson, *J. Org. Chem.*, 1969, **34**, 1444.