Aryl Migration Reactions in the Alkaline Hydrolysis of Vinylphosphonium Ions. The Role of the Electron Sink and the Effects of Substitution at the Migration Terminus

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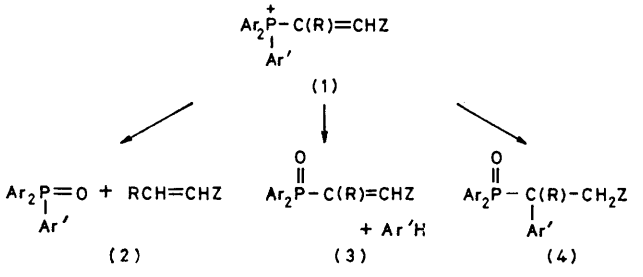
The vinylphosphonium ions $Ar_2\overset{+}{P}(Ar')C(R)=CHZ$ (1; Ar = Ph; Ar' = *o*-chlorophenyl, *m*-trifluoromethylphenyl, 2-furyl, 2-thienyl, and 1-methylpyrrol-2-yl; R = H; and Z = CO_2Et) (encountered as intermediates in the reactions of the phosphines Ar_2PAr' with ethyl propiolate in the presence of water) undergo hydrolysis with predominant migration of Ar' from phosphorus to adjacent carbon to form $Ar_2P(O)C(R)(Ar')CH_2Z$ (4) in contrast to the predominant loss of Ar' which occurs in the hydrolysis of related ions in which Z = Ph. The vinylphosphonium ions (1; Ar = Ph, Ar' = *o*-chlorophenyl or 2-thienyl, R = Ph, and Z = CO_2Et) (from the reaction of Ar_2PAr' with ethyl phenylpropiolate in the presence of water) undergo hydrolysis with loss of either the vinylic group or the group Ar'. It is suggested that when R = Ph, the migration reaction is inhibited as a result of steric crowding in the intermediate phosphorane. When this is reduced, as in the hydrolysis of the phosphonium ion derived from 5-methyldibenzophosphole and ethyl phenylpropiolate, predominant migration occurs even when R = Ph. The implications of this result for a recently suggested alternative mechanism of the aryl migration reaction are considered.

THE alkaline hydrolysis of vinylphosphonium ions (1) may proceed with (i) loss of the vinylic group to form a simple arylphosphine oxide (2) and an alkene,[1,2] (ii) complete loss of an aryl substituent from phosphorus to form a vinylphosphine oxide (3),[3,4] or (iii) migration of the aryl substituent most stable as the carbanion from phosphorus to adjacent carbon to form the rearranged phosphine oxide (4).[5-7]



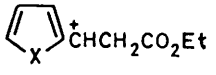
The course of the reaction depends on (i) the nature of the electron sink Z, (ii) the nature of the aryl groups bound to phosphorus, and (iii) the nature of the group R. When the group Z is able to stabilise an adjacent forming carbanion (*e.g.* COAr,[8] SR,[9] or CO_2Me [6]) predominant migration of a phenyl group has been observed when R = H. When Z is less strongly electron-withdrawing (*e.g.* OR), phenyl rearrangement does not occur, and simple loss of the phenyl group or the vinyl group occurs, depending on the conditions.[9] When Z = Ph (and R = H), the course of decomposition depends very much on the stability of the carbanion derived from the group Ar'. Carbanions of moderate stability (*e.g.* $C_6H_5^-$, *p*-$MeOC_6H_4^-$, and *m*-$ClC_6H_4^-$) require the additional stabilisation of negative charge afforded in the transition state of the rearrangement reaction, as a result of the involvement of the group Z, and thus preferentially migrate from phosphorus to adjacent carbon. For carbanions of greater stability, *e.g.* *m*-$CF_3C_6H_4^-$, simple cleavage of group Ar' is the preferred course, leading to a vinylphosphine oxide (3).[4] In this paper, we report further studies of the role of the group Z in influencing either loss or rearrangement of the group Ar'; in addition, we have investigated the influence of the group R at the potential migration terminus. The latter aspect has so far received little study.

Throughout this work we have made the reasonable assumption (based on earlier work [1,6]) that the vinylphosphonium ions (1) are encountered as intermediates in the reactions of appropriate tertiary phosphines with either ethyl propiolate or ethyl phenylpropiolate in the presence of water in tetrahydrofuran (THF) solution.

Whereas when Z = Ph and R = H, hydrolysis of vinylphosphonium ions in which Ar = Ph and Ar' = *o*-ClC_6H_4 or *m*-$CF_3C_6H_4$ results in the formation of the vinylphosphine oxide (3; Ar = Z = Ph, R = H),[4] we now find that when Z = CO_2Et, the related ions undergo hydrolysis with exclusive migration of the *o*-chlorophenyl or *m*-trifluoromethylphenyl group to form the rearrangement products (4; Ar = Z = Ph, R = H, Ar' = *o*-ClC_6H_4 or *m*-$CF_3C_6H_4$). Support for the migration of the *o*-chlorophenyl or *m*-trifluoromethylphenyl groups was adduced from the mass spectra of the rearrangement products, both of which showed a base peak at *m/e* 201 corresponding to the $[Ph_2PO]^+$ fragment. Clearly, replacement of phenyl by CO_2Et as the electron-accepting group stabilises the transition state for migration relative to that for complete loss of the group Ar', and thus the nature of the electron sink Z appears to be the dominating factor, rather than the nature of the group Ar', in controlling the outcome of the hydrolysis reactions.

Support for this view was forthcoming from studies of the hydrolysis of a similar range of ions in which Ar' = 2-furyl, 2-thienyl, and 1-methylpyrrol-2-yl. Our earlier work on the hydrolysis of heteroarylphosphonium salts has shown that the above 2-heteroaryl groups are readily cleaved from phosphorus, as a result of the stabilisation of the forming 2-heteroaryl carbanions by the adjacent electronegative heteroatoms.[10-12] In keeping with these observations, we have previously noted the complete

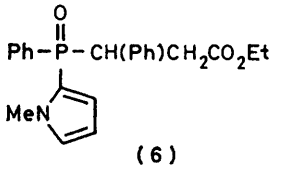
loss of 2-furyl and 1-methylpyrrol-2-yl groups from certain vinylphosphonium ions in which Z = Ph.[4] We now find that when the electron-accepting group Z = CO_2Et, hydrolysis of the ions (1; Ar = Ph, R = H, and Ar′ = 2-furyl or 2-thienyl) takes place with the predominant formation of the rearrangement products (4), migration of a heteroaryl group from phosphorus to carbon having occurred. The base peak in the mass spectrum of each of the above heteroaryl rearrangement products occurred at *m/e* 201, corresponding to the $[Ph_2PO]^+$ fragment. Of lower abundance in each spectrum was a peak corresponding to the remainder of the molecule (5). Ions corresponding to the fragment-



(5)

ation of the ester side-chain were also observed in each case.

From the hydrolysis of (1; Ar = Ph, R = H, and Ar′ = 1-methylpyrrol-2-yl), two isomeric rearrangement products (6) and (7) were isolated, corresponding to migration of either the phenyl group or the 1-methylpyrrol-2-yl group. The mass spectrum of (6) showed a base peak at *m/e* 204, corresponding to the $[Ph(C_5H_6N)PO]^+$ fragment. In contrast, that of (7) showed a base peak at *m/e* 180, corresponding to the fragment (5; X = NMe). Also observed was an ion at *m/e* 201 corresponding to $[Ph_2PO]^+$. Further support for the above structural assignments was adduced from the ^1H n.m.r. spectra. That of (6) showed a singlet at δ 3.72, corresponding to the N-Me group of a 1-methylpyrrol-2-yl group attached to P=O. A similar signal at δ 3.72 is shown in the spectrum of 1-methylpyrrol-2-yldiphenylphosphine oxide. In contrast, the spectrum of (7) showed an N-Me signal at δ 3.12 consistent with



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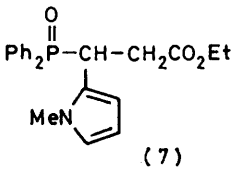


(7)

the greater shielding expected for the pyrrolyl substituent attached to carbon.

Only in the case of the ion bearing a 2-thienyl substituent at phosphorus was the vinylphosphine oxide (3; Ar = Ph, R = H, Z = CO_2Et), arising from direct loss of the heteroaryl substituent from phosphorus, isolated. This compound was obtained only in very small quantities, indicating that this mode of hydrolysis is much less favoured than that leading to the rearrangement products for the above salts in which Z = CO_2Et, compared to those in which Z = Ph.

The products of hydrolysis of the above vinylphosphonium ions are consistent with previous findings concerning the relative stabilities of the forming 2-heteroaryl and phenyl carbanions. As indicated by their relative ease of cleavage from phosphorus in the hydrolysis of simple phosphonium salts, the relative stabilities of the forming carbanions have been shown to be in the order 2-thienyl > 2-furyl ≫ 1-methylpyrrol-2-yl > phenyl.[10-12]

The formation of the vinylphosphine oxide in the hydrolysis of the above 2-thienylphosphonium ion can be attributed to the greater stability of the forming 2-thienyl carbanion, and that direct loss of the 2-thienyl group is able to compete (albeit to a small extent only) with the migration reaction, even when Z = CO_2Et.

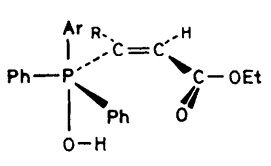
In accordance with their carbanionic stabilities, both the 2-furyl and 2-thienyl groups migrate from phosphorus to carbon in preference to phenyl. However, in the case of the 1-methyl-pyrrol-2-ylphosphonium ion, competitive migration of the pyrrolyl and phenyl groups occurs. It is of interest that in the hydrolysis of the corresponding ion in which Z = Ph, loss of only the 1-methylpyrrolyl group was observed.[4] The competing migration of both the pyrrolyl and phenyl groups when Z = CO_2Et points to a levelling effect by the group Z on the energies of the transition states leading to rearrangement of these groups.

We have also explored the influence of the group R at the potential migration terminus. It has been shown that the ion (1; Ar = Ar′ = R = Ph, Z = CO_2Me) undergoes hydrolysis with loss of the vinylic substituent to give triphenylphosphine oxide and methyl *trans*-cinnamate,[1] whereas hydrolysis of the related ion in which R = Me gives rise to the rearrangement product (4; Ar = Ar′ = Ph, R = Me, Z = CO_2Me). Although this product was isolated in only 10% yield from the reaction of triphenylphosphine with methyl but-2-ynoate and water in THF solution, no other products were detected. The small yield of the rearranged product was attributed to crowding at the centre which receives the migrating group.[6]

We now find that whereas the ions (1; Ar = Ph, Ar′ = *o*-chlorophenyl or 2-thienyl, R = H, and Z = CO_2Et) undergo hydrolysis with predominant rearrangement, the related species in which R = Ph undergo hydrolysis with predominant loss of the substituted vinyl group; in each case, the vinylphosphine oxide (3; Ar = R = Ph, Z = CO_2Et) was isolated as a minor product arising from loss of Ar′. Clearly the phenyl group at the migration terminus is inhibiting the migration reaction.

On the assumption that the potential migrating group occupies the apical position of an intermediate trigonal bipyramidal hydroxyphosphorane, and that the vinylic group occupies an equatorial site, the most favourable situation for migration would be when the carbon 2*p* orbitals which overlap to form the π bond of the vinyl group are in the apical plane. A model of the assumed hydroxyphosphorane intermediate (8) shows that when R = phenyl, there is considerable steric crowding between R and one of the equatorial phenyl groups, and also to some extent between the ethoxycarbonyl group and a second equatorial phenyl group. This steric

crowding is relieved to some extent if the R phenyl group is replaced by methyl or preferably by hydrogen, or if the vinyl group is twisted out of the equatorial plane. However, the latter will diminish the chances of migration of the apical ligand. Direct loss of the apical ligand clearly reduces steric crowding.



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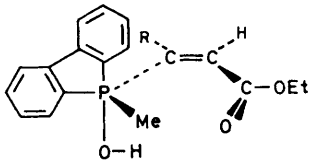
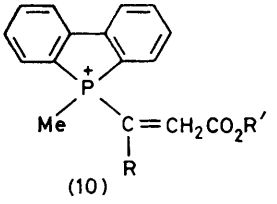


(9)

Following this argument, we reasoned that if steric crowding in the hydroxyphosphorane could be reduced, *e.g.* by incorporation of the apical-equatorial aryl groups into the planar dibenzophosphole system, and replacement of the remaining equatorial aryl group by methyl, then, as indicated by models of the intermediate phosphorane (9), rearrangement might be facilitated even when R = Ph. This proved to be so. Thus, hydrolysis of the ion (10; R = Ph, R′ = Et) proceeded with the predominant formation of the ring-expanded product (11; R = Ph, R′ = Et), isolated in 92% overall yield



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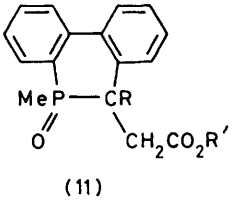
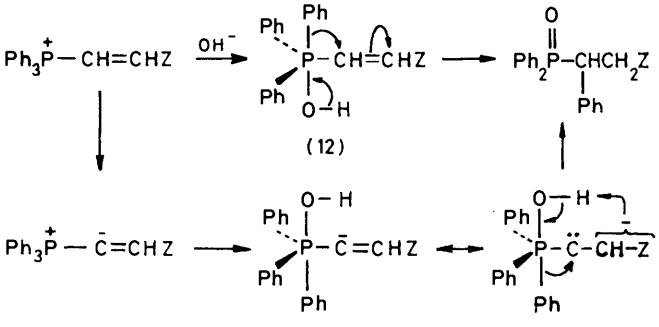


(11)

from the reaction of 5-methyldibenzophosphole with ethyl phenylpropiolate in wet THF. The u.v. spectrum of (11; R = Ph, R′ = Et) is very similar to the related compound (11; R = H, R′ = Me) isolated by Richards and Tebby [13] from the reaction of 5-methyldibenzophosphole and methyl propiolate in the presence of water. The ^{1}H n.m.r. spectrum of (11; R = Ph, R′ = Et) showed the expected resonances, including an ABX pattern for the diastereotopic protons of the exocyclic CH_2CO_2R' group.



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This result is of significance in connection with a recently proposed alternative mechanism for the aryl migration reaction in the hydrolysis of vinylphosphonium ions. The hitherto accepted mechanism,[6] involving the intramolecular collapse of the hydroxyphosphorane (12), has been criticised, and an alternative route involving the ylid (13) and the carbenoid phosphorane (14) suggested.[9]

Clearly this mechanism could only apply when group R in (1) is hydrogen. Our above observation of aryl migration when R = Ph, together with Richards and Tebby's earlier example [6] when R = Me, make the above alternative mechanism seem unlikely to be correct.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded at 60 MHz with a JEOL spectrometer (Me_4Si as internal standard). Mass spectra were recorded at 70 eV with an AEI MS30 spectrometer.

Synthesis of Phosphines.—2-Furyldiphenylphosphine,[14] diphenyl(2-thienyl)phosphine,[15] (1-methylpyrrol-2-yl)diphenylphosphine,[12] diphenyl(3-trifluoromethylphenyl)phosphine,[4] (2-chlorophenyl)diphenylphosphine,[16] and 5-methyldibenzophosphole [17] were prepared as described in the literature.

Reactions of Phosphines with Acetylenic Esters.—General procedure. The phosphine (0.2 g), the appropriate acetylenic ester (0.2 g, >1 mol), and water (4 drops) were dissolved in THF (3 cm^3) and the resulting solution heated under reflux for up to 24 h. The solution was then evaporated, and the residue subjected to preparative t.l.c. on 20 × 20 cm preparative plates coated (2 mm) with Kieselgel HF 256 (solvent, 1 : 1 hexane–ethyl acetate). Individual bands were extracted with ethanol to yield the phosphine oxide products.

Reactions with Ethyl Propiolate.—(2-Chlorophenyl)diphenylphosphine. This gave solely the rearrangement product, 1-(2-chlorophenyl)-2-(ethoxycarbonyl)ethyldiphenylphosphine oxide (4; Ar = Ph, Ar′ = 2-chlorophenyl, R = H, Z = CO_2Et) (70%) as an oil, which resisted crystallisation; δ($CDCl_3$): 8.4—7.0 (m, 14 ArH), 4.9 (m, 1 H), 3.95 (q, 2 H), 3.1 (m, 2 H), and 1.1 (t, 3 H); *m/e*: 414, 412 (M^+), 386, 384 (M − C_2H_4), 377 (M − Cl), 369, 367 (M − EtO), and 201 (Ph_2PO) (base peak). This was characterised further by alkaline hydrolysis to the corresponding *carboxylic acid* (4; Ar = Ph, Ar′ = 2-chlorophenyl, R = H, and Z = CO_2H), which had m.p. 224 °C (ex. hexane–EtOAc–EtOH) (Found: C, 66.05; H, 5.0. $C_{21}H_{18}ClO_3P$ requires C, 65.55; H, 4.75%); δ($CDCl_3$): 8.7—6.7 (m, 14 ArH), 5.1—4.6 (m, 1 H), and 3.4—2.7 (m, 2 H); *m/e*: 386, 384 (M^+), 349 (M − Cl), and 201 (Ph_2PO) (base peak).

Diphenyl-(3-trifluoromethylphenyl)phosphine. This reaction gave solely the rearrangement product, *2-(ethoxycarbonyl)-1-(3-trifluoromethylphenyl)ethyldiphenylphosphine oxide* (4; Ar = Ph, Ar′ = 3-$CF_3C_6H_4$, R = H, Z = CO_2Et), m.p. 160 °C (ex. hexane–EtOH) (Found: C, 64.4; H, 5.05. $C_{24}H_{22}F_3O_3P$ requires C, 64.55; H, 5.0%), δ($CDCl_3$): 8.5—7.1 (m, 14 ArH), 4.5—3.7 (m, 1 H, and q, 2 H), 3.3—2.7 (m, 2 H), and 1.0 (t, 3 H); *m/e* 418 (M − C_2H_4) and 201 (Ph_2PO) (base peak).

Diphenyl(2-thienyl)phosphine. The major product was the rearrangement product, *[2-(ethoxycarbonyl)-1-(2-thienyl)-ethyl]diphenylphosphine oxide* (4; Ar = Ph, Ar′ = 2-thienyl, R = H, and Z = CO_2Et) (45%), m.p. 154 °C (ex. hexane–EtOAc) (Found: C, 65.5; H, 5.5. $C_{21}H_{21}O_3PS$ requires C, 65.6; H, 5.5%), δ($CDCl_3$): 8.3—6.8 (m, 13

ArH), 4.75—3.8 (m, 1 H and q, 2 H), 3.0 (t, 2 H), and 1.1 (t, 3 H); *m/e*: 201 (Ph_2PO) (base peak) and 183 ($C_4H_3SCHCH_2CO_2Et$). Also isolated, as an oil which resisted crystallisation, was diphenyl[(2-ethoxycarbonyl)vinyl]phosphine oxide (3; Ar = Ph, R = H, Z = CO_2Et) (10%); δ($CDCl_3$): 8.2—7.2 (m, 10 ArH), 7.05 (d, 1 H), 6.6br (s, 1 H), 4.0 (q, 2 H), and 1.1 (t, 3 H); *m/e*: 300 (M^+), 272 ($M - C_2H_4$), 255 (M — OEt), and 201 (Ph_2PO).

2-Furyldiphenylphosphine. This gave solely the rearrangement product, 2-(ethoxycarbonyl)-1-(2-furyl)ethyldiphenylphosphine oxide (4; Ar = Ph, Ar′ = 2-furyl, R = H, and Z = CO_2Et) (73%), as an oil, which resisted crystallisation; δ($CDCl_3$): 8.1—7.0 (m, 11 ArH), 6.15 (m, 2 ArH), 4.7—3.75 (m, 1 H and q, 2 H), 3.0 (t, 2 H), and 1.05 (t, 3 H); *m/e*: 368 (M^+), 340 ($M - C_2H_4$), 323 (M — OEt), 201 (Ph_2PO) base peak), and 167 ($C_4H_3OCHCH_2CO_2Et$).

(1-Methylpyrrol-2-yl)diphenylphosphine. This gave the following isomeric rearrangement products, initially as a mixture from preparative t.l.c., but subsequently separated by crystallisation: *[2-(ethoxycarbonyl)-1-(1-methylpyrrol-2-yl)ethyl]diphenylphosphine oxide* (4; Ar = Ph, Ar′ = 1-methylpyrrol-2-yl, R = H, and Z = CO_2Et), as plates, m.p. 168—170 °C (ex. EtOAc–hexane) (Found: C, 69.3; H, 6.45; N, 3.75. $C_{22}H_{24}NO_3P$ requires C, 69.25; H, 6.35; N, 3.65%); δ($CDCl_3$): 8.1—7.2 (10 ArH), 6.5 (m, 1 H), 6.15 (m, 2 H), 4.4—3.7 (m, 1 H and q, 2 H), 3.12 (s, 3 H, NMe), and 1.1 (t, 3 H); *m/e*: 381 (M^+); 353 ($M - C_2H_4$), 336 (M — OEt), 201 (Ph_2PO), and 180 ($C_5H_6NCHCH_2CO_2Et$) (base peak). Additional of hexane to the mother liquors from the crystallisation of the above gave *[2-(ethoxycarbonyl)-1-phenylethyl](1-methylpyrrol-2-yl)-phenylphosphine oxide* (6), as needles, m.p. 148—150 °C (Found: C, 68.95; H, 6.25; N, 3.95. $C_{22}H_{24}NO_3P$ requires C, 69.25; H, 6.35; N, 3.65%), δ($CDCl_3$): 7.7—7.1 (m, 10 ArH), 6.93 (m, 2 H), 6.35 (m, 1 H), 4.4—3.6 (m, 1 H, and q, 2 H), 3.72 (s, 3 H, NMe), 3.3 (m, 2 H), and 1.17 (t, 3 H); *m/e*: 381 (M^+); 353 ($M - C_2H_4$), 336 (M — OEt), and 204 [$C_5H_6NP(O)Ph$] (base peak).

Reactions with Ethyl Phenylpropiolate.—Diphenyl-(2-thienyl)phosphine. This gave, as the major product, diphenyl-(2-thienyl)phosphine oxide (60%), m.p. 117 °C, identical with an authentic sample; [15] also isolated (24%) was *diphenyl-[2-(ethoxycarbonyl)-1-phenyl-vinyl]phosphine oxide* (3; Ar = Ph, R = Ph, Z = CO_2Et), m.p. 133 °C (ex. EtOAc–hexane) (Found: C, 73.3; H, 5.65. $C_{23}H_{21}O_3P$ requires C, 73.35; H, 5.6%), δ($CDCl_3$): 8.0—6.6 (m, 16 H), 4.0 (q, 2 H), and 1.0 (t, 3 H); *m/e*: 376 (M^+).

(2-Chlorophenyl)diphenylphosphine. This gave, as the major product, *(2-chlorophenyl)diphenylphosphine oxide* (43%), m.p. 95—97 °C (ex. EtOAc–hexane) (Found: C, 68.65; H, 4.65. $C_{18}H_{14}ClOP$ requires C, 69.1; H, 4.5%), identical with the product of oxidation of the parent phosphine with hydrogen peroxide. Also isolated was *diphenyl-[2(ethoxycarbonyl)-1-phenylvinyl]phosphine oxide* (19%), m.p. 133 °C (ex. EtOAc–hexane) (Found: C, 73.45; H, 5.65. $C_{23}H_{21}O_3P$ requires C, 73.35; H, 5.6%), identical with that isolated above.

5-Methyldibenzophosphole. This gave as the sole product, *6-ethoxycarbonylmethyl-5-methyl-6-phenyl-5,6-dihydrodibenzo*[b,d]*phosphorin 5-oxide* (11; R = Ph, R′ = Et) (92%), m.p. 138 °C (ex. EtOAc–hexane) (Found: C, 73.95; H, 6.0. $C_{24}H_{23}O_3P$ requires C, 73.8; H, 5.95%); δ($CDCl_3$): 8.3—7.1 (m, 13 ArH), 4.5—3.2 (m, 2 H and q, 2 H), 1.47 [d, 3 H, $^2J_{PCH}$ 13.5 Hz, P(O)Me], and 1.0 (t, 3 H); *m/e*: 390 (M^+), 362 ($M - C_2H_4$), 345 (M — OEt) and 241 (base peak); $\lambda_{max.}$ (EtOH): 218 (ε 32 948), 230 infl. (ε 17 146), 272 (ε 8 069), and 286 infl. (ε 5 379).

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