

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

The Steric Course of the Claisen Rearrangement

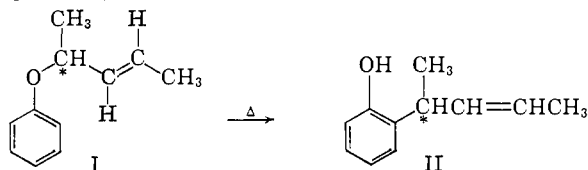
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An infrared study of the stereochemistry attending the Claisen rearrangement of *cis*- and *trans*- α,γ -dimethylallyl and two other related vinyl ethers has shown that the reaction produces essentially only *trans* substituted allylacetaldehydes. The double bond in the *o*-Claisen rearrangement product of *trans*- α,γ -dimethylallyl phenyl ether has also been demonstrated by infrared absorption to be predominantly *trans*. The transition state geometry of the Claisen rearrangement implied by these findings is discussed.

Introduction

Viewed in relation to its intramolecular character, the Claisen rearrangement¹ of the phenyl or vinyl ether of a substituted allylic alcohol often poses an interesting and rather subtle problem of preferential transition state orientation. For example, the finding of Alexander and Klüber² that optical activity was present in the 2-(α,γ -dimethylallyl)-phenol (II) formed by rearrangement of (-)-*trans*- α,γ -dimethylallyl phenyl ether (I) indicates that it is possible for a considerable degree of stereospecificity to attend this type of reaction.³



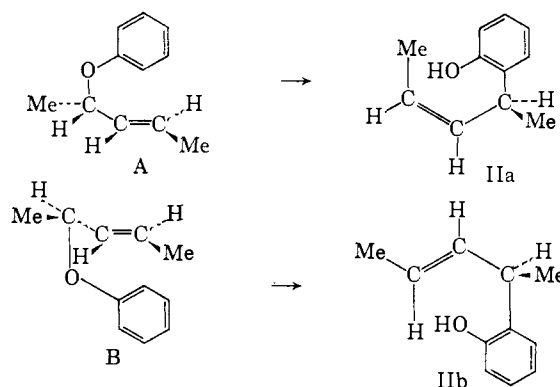
In an effort to discern the precise nature of the stereochemical relationship between I and II, Alexander and Klüber² and also Hart⁴ have proposed that the reaction proceeds preferentially through the transition-state approach A rather than B (or their mirror images). This interpretation was based on the reasoning that rearrangement issuing from conformation A introduces less steric interaction of substituents in the transition state than does that arising from orientation B. It was also observed that 2-(α,γ -dimethylallyl)-phenol (II) of the same sign (*dextro*), but not magnitude, of rotation as that produced in the rearrangement also resulted from the direct alkylation of phenol with the (-)- α,γ -dimethylallyl chloride which was used to prepare the levorotatory ether I. This fact was taken by Hart⁴ to

(1) Reviewed by D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. 1; see also (a) D. J. Cram in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 5, pp. 295-303; (b) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, Chap. 15, pp. 644-649.

(2) E. R. Alexander and R. W. Klüber, *THIS JOURNAL*, **73**, 4304 (1951).

(3) Since there is a strong possibility that partial racemization may have taken place in the preparation of I from (+)-*trans*- α,γ -dimethylallyl alcohol *via* alkylation of the corresponding chloride, the optical purity of I, and hence of II, should probably be considered with reserve in this work of Alexander and Klüber (see S. J. Rhoads, R. Raulins and R. D. Reynolds, *ibid.*, **76**, 3456 (1954); also footnote 5). In addition, it is also conceivable, but probably not very likely in view of its comparative stability, that partial racemization of II may have occurred during or after its formation, perhaps by a mechanism involving reversal of the Claisen rearrangement step itself [*cf.* W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, *ibid.*, **80**, 3271 (1958) and references cited there; see also F. Kalberer, K. Schmid and H. Schmid, *Helv. Chim. Acta*, **39**, 555 (1956)].

(4) H. Hart, *THIS JOURNAL*, **76**, 4033 (1954); *cf.* ref. 1b.



mean that the configuration of the asymmetric center in II with respect to the phenyl ring was the *same* as that in I with respect to the ether function.³ In this event it follows that the geometry of the rearrangement would be that shown in A \rightarrow IIa rather than in B \rightarrow IIb.

On the other hand, in taking note of these arguments, Goering and Jacobson⁶ have pointed out recently that the kinetic and transition-state similarities of the *o*-Claisen rearrangement and the intramolecular (S_Ni') rearrangement of allylic esters (*e.g.*, III \rightarrow IV) suggest that the configuration of the asymmetric center in the reactant relative to that in the product in the Claisen rearrangement under discussion *should, in fact, be opposite* to each other, just as has been demonstrated⁷ to be the case in the S_Ni' allylic ester rearrangement. This, of course, is to be expected if the transition-state approach B applies rather than A in the rearrangement of I to II.

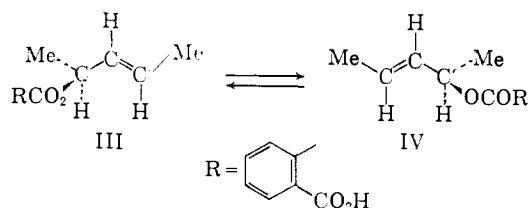
(5) This conclusion rests on the assumption that simple S_N2 (or exclusive S_N2') alkylation occurred in *both* the preparation of I and the direct formation of II by C-alkylation of phenol. However, the dextrorotatory character of the two preparations of II (from the Claisen rearrangement and the C-alkylation of phenol) could, conceivably, be the result of a preponderance of S_N2' alkylation in *either* the preparation of I or the direct formation of II. Under these circumstances the configurations of the asymmetric center in I and in II would actually be *opposite* to each other, instead of the same.

Relevant discussions of steric and reagent-type aspects of the S_N2' reaction have been presented by G. Stork and W. N. White, *ibid.*, **78**, 4609 (1956); by W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951); and by W. G. Young, R. A. Clement and C.-H. Shih, *ibid.*, **77**, 3061 (1955).

(6) H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1958); *cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. X, pp. 596-600.

(7) H. L. Goering and R. W. Greiner, *THIS JOURNAL*, **79**, 3464 (1957). See also F. F. Caserio, G. E. Dennis, R. H. DeWolfe and W. G. Young, *ibid.*, **77**, 4182 (1955).

In this connection it should be noted that allylic rearrangements involving a *cis* \rightleftharpoons *trans* conversion would be expected to give rise to effective "retention" rather than "inversion" of configuration at the asymmetric center.



A further stereochemical consequence of the transition-state approach A is that the product (IIa) arising from it would possess the less stable *cis* configuration about the olefinic bond, whereas that (IIb) resulting from B would have the more stable *trans* arrangement about the double bond. This has also been recognized^{6,7} with respect to the $\text{S}_{\text{N}}1'$ rearrangement of substituted allylic esters of the type III and IV, in which the geometry of the product has been demonstrated⁷ to be *trans*.⁸ In view of this, barring the possibility of subsequent *cis* \rightarrow *trans* isomerization of the initially formed product (which conceivably could occur, for example, by a mechanism involving reversal⁸ of the rearrangement step), it would seem all the more reasonable to expect that the more stable *trans* isomer IIb, rather than the less stable *cis* one IIa, should be the stereochemically preferred result of the *o*-Claisen rearrangement of I.

Unfortunately, the configuration of the double bond in II was not determined in the investigation of Alexander and Klüber,² nor was it discussed by Hart⁴ in his subsequent analysis of this work. Although Goering and Jacobson⁵ have indicated their intention of re-examining the relative configurations of the asymmetric center in I and II, it appeared to the present author that a knowledge of the geometry of the double bond in II and similar Claisen rearrangement products would also be of value for the purpose of assessing the stereochemical course of such reactions. In the present investigation, this aspect of the Claisen rearrangement has been explored in the rearrangement of a number of substituted open-chain allyl vinyl ethers to the corresponding substituted allylacetaldehydes. In addition, the configuration of the double bond in the substituted phenolic product afforded by rearrangement of the racemic form of I has also been examined.^{8a}

Results and Discussion

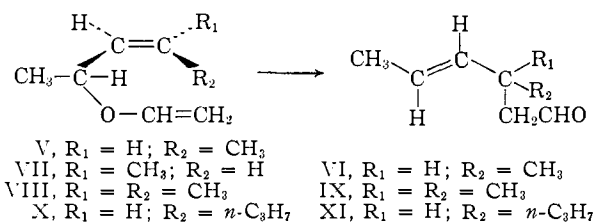
Four simple yet representative substituted allyl vinyl ethers were synthesized for the purposes of

(8) A further example of a substituted allylic ester isomerization of this nature (but taking place in the gas phase) has been disclosed very recently by F. L. Greenwood [*J. Org. Chem.*, **24**, 1735 (1959)] in the interconversion of 2-acetoxy-*trans*-3-heptene and 4-acetoxy-*trans*-2-heptene at 350–370°. In the products the *trans*-esters were found to be greatly predominant, but some of the *cis*-esters were also detectable.

(8a) NOTE ADDED IN PROOF (May 17, 1960).—The present work was first reported by the author at the Eleventh Annual Kansas City Chemistry Conference, November 6, 1959, and later at the Cleveland Meeting of the American Chemical Society, April 11, 1960 (Abstracts, p. 16-O). Very recently, in a preliminary communication on the stereochemistry of the rearrangement of *cis*- as well as *trans*- α,γ -dimethylallyl phenyl ether, E. N. Marvell and J. L. Stephenson, *J. Org. Chem.*, **25**, 676 (1960), have described a similar approach to the problem and have obtained results comparable to those found here. Further recent evidence bearing on the configuration of the transition state in the *o*-Claisen rearrangement has been reported by B. E. Norcross and W. N. White (Abstracts of Papers Presented at the Cleveland Meeting of the American Chemical Society, April 5–14, 1960, p. 15-O).

the present study: (\pm)-*cis*- and (\pm)-*trans*- α,γ -dimethylallyl vinyl ether (V and VII, respectively), (\pm)- α,γ,γ -trimethylallyl vinyl ether (VIII) and (\pm)-*cis*- α -methyl- γ -propylallyl vinyl ether (X). These were conveniently prepared from the corresponding allylic alcohols by the vinyl transesterification procedure of Watanabe and Conlon⁹ and were obtained in analytically pure condition after several distillations from sodium at reduced pressure.

When heated in sealed tubes at 170–180° for 15–20 min. these ethers were converted cleanly and in good yields to the corresponding substituted allylacetaldehydes (VI, IX and XI, respectively). These proved, on the basis of their infrared ab-



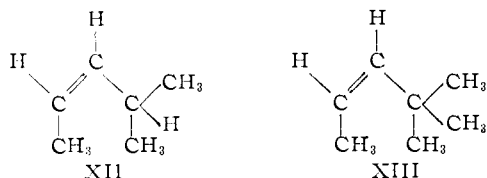
sorption, to be predominantly, if not entirely, the *trans* isomers shown. Strong *trans* disubstituted olefin absorption¹⁰ was present in their spectra at 10.3–10.4 μ ; *cis*-olefin absorption, expected at 6.1 and 13–15 μ ,¹⁰ was completely absent. In addition to being relatively homogeneous according to gas chromatographic analysis, each gave a quite sharp melting semicarbazone and 2,4-dinitrophenylhydrazone. By hydrogenation over palladium-on-charcoal they afforded the corresponding saturated aldehydes, which in turn also furnished sharp melting derivatives. As an illustration of a potentially useful synthetic application of the sequence, the unsaturated and saturated carboxylic acids derived from VI and IX were also prepared.

The fact that *trans* unsaturated aldehydes were obtained by rearrangement of both *cis* and *trans* substituted allyl vinyl ethers suggests that the transition state orientation in the reaction is strongly influenced by factors relating to product stability. However, the possibility that these results are due to isomerization of the *cis*-allyl vinyl ethers to the *trans* forms prior to rearrangement, or that the initially produced products were *cis* (or mixtures of *cis* and *trans*) isomers, which then underwent isomerization to the observed all-*trans* products during the time allotted for the reaction, must still be reckoned with. In another series of experiments, the *cis*-vinyl ethers V and X were found to be recovered unchanged when the rearrangement was conducted to 80% completion. Hence the first of these alternative possibilities would not appear to be operative to any significant extent. For assessment of the second alternative, at least in part, since the corresponding *cis* substituted allylacetaldehydes are not readily accessible, an examination was made of the thermal stability of two high-purity *cis*-olefins structurally very similar to these unsaturated aldehydes. American

(9) W. H. Watanabe and L. E. Conlon, *THIS JOURNAL*, **79**, 2828 (1957).

(10) Cf. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edition, Methuen and Co., Ltd., London, 1958, Chap. 3.

Petroleum Institute samples¹¹ of 4-methyl-*cis*-2-pentene (XII) and 4,4-dimethyl-*cis*-2-pentene (XIII) were subjected not only to the conditions of the rearrangement (180° for 20 min.), but also to temperatures up to 210° for 2 hr. In keeping with



the known stability of *cis*-2-butene at such temperatures,¹² these olefins were recovered without detectable conversion to *trans* isomers (no increase in absorption in the region 10.3–10.5 μ). For comparison purposes, pure 4-methyl-*trans*-2-pentene and 4,4-dimethyl-*trans*-2-pentene¹¹ were similarly examined.

In the light of the foregoing results, and in view of the essentially neutral character of the reactants and products involved in the rearrangement of allyl vinyl ethers to allylacetaldehydes, it would appear highly unlikely that the *trans* unsaturated aldehydes isolated from the rearrangements described here arose by any form of bond isomerization rather than directly from the rearrangement process itself.¹³ Hence, at least on the basis of these simple, typical examples, it can be concluded that the preferred stereochemistry of the Claisen rearrangement of substituted open-chain allyl vinyl ethers is that in which the thermodynamically more stable (*trans*) configuration of the double bond strongly predominates in the product. In all likelihood, as more cases are examined, this will probably prove to be the general rule.

Finally, as an adjunct to the preceding work, the rearrangement of (\pm)-*trans*- α,γ -dimethylallyl phenyl ether (I) to (\pm)-2-(α,γ -dimethylallyl)-phenol (II) was examined with a view to the determination of the configuration of the double bond in II. In agreement with the findings in the rearrangement of substituted allyl vinyl ethers, a *trans* disubstituted double bond was shown by infrared assay to be present in II (strong absorption at 10.3 μ , virtually none in the 13–15 μ region attributable to *cis* isomer).¹⁰ Again it is conceivable that an initially formed *cis* product underwent isomerization to the *trans* isomer, perhaps by an equilibration process involving reversal of the rearrangement step,³ but this possibility appears rather unlikely, or at least of minor consequence in this case, since appreciable optical activity is retained in the product formed by rearrangement of the optically

active form of I under the same conditions.² The stability of the high-purity *cis*-olefins XII and XIII in the presence of one molar equivalent of ordinary phenol under the conditions of the rearrangement (1 hr. at 195°) and at temperatures up to 210° for 1 hr. was also examined. As before, neither of the recovered olefins bore evidence detectable by infrared absorption of having undergone conversion to a *trans* isomer.

On the basis of these results it can be concluded therefore that the preferred steric course of the *o*-Claisen rearrangement of I to II is that pictured in the pathway B→IIb rather than A→IIa. Indirectly, these results also support the tentative suggestion of Goering and Jacobson⁶ that the configuration of the asymmetric center in II is enantiomeric to that of I in the optically active series.

Experimental¹⁴

3-Alken-2-ols.—*cis*-3-Penten-2-ol, b.p. 53–55° (25 mm.), n_D^{20} 1.4272, and *cis*-3-hepten-2-ol, b.p. 69–70° (22 mm.), n_D^{20} 1.4350, were prepared on a 0.5-mole scale by semi-hydrogenation of the corresponding ethynylcarbinols in ethanol solution over the Lindlar¹⁵ catalyst. Their infrared spectra had a band of moderate intensity at 6.1 μ and a very strong one at 13.3–13.5 μ (1,2-disubstituted *cis*-olefin absorption).¹⁰ The required ethynylcarbinols were in turn obtained from acetaldehyde and the appropriate alkylacetylene by the Grignard method.¹⁶ *trans*-3-Penten-2-ol, b.p. 50–52° (25 mm.), n_D^{20} 1.4245, was prepared by the procedure described in reference 17. Its infrared spectrum had a strong band at 10.3 μ ,¹⁰ but no absorption in the 6.1 or 13–15 μ regions. 4-Methyl-3-penten-2-ol, b.p. 62–64° (25 mm.), n_D^{20} 1.4310, was obtained by reduction of purified¹⁸ mesityl oxide with excess lithium borohydride at 0° for 8 hr. Its infrared spectrum had strong absorption at 12.3 μ , corresponding to a trisubstituted olefinic linkage.¹⁰ A very weak band at 11.2 μ suggested the presence of a small amount of the isomeric 4-methyl-4-penten-2-ol.¹⁰

Vinyl Ethers.—Conversion of the preceding alkenols to the corresponding vinyl ethers, V, X, VII and VIII, respectively, was effected by the transesterification procedure (method B) of Watanabe and Conlon⁹ on a 0.25-mole scale. For most effective results it was necessary to use ethyl vinyl ether that had been redistilled from sodium and mercuric acetate that had been recrystallized several times from ethanol. Isolation of the desired products by distillation at reduced pressure was facilitated by the fact that their boiling points were about 15° lower than those of the starting alcohols. The yields ranged from 35 to 45%. Several redistillations from sodium at reduced pressure furnished the purified vinyl ethers as colorless, mobile liquids, whose properties and analyses were

Vinyl ether	B.p., °C.		n_D^{20}	Carbon, %		Hydrogen, %	
	°C.	Mm.		Calcd.	Found	Calcd.	Found
V	36–37	23	1.4230	74.95	75.12	10.78	10.90
VII	35–36	25	1.4203	74.95	75.24	10.78	11.02
VIII	45–46	25	1.4285	76.14	75.86	11.18	11.37
X	55–56	22	1.4320	77.09	77.35	11.50	11.64

(14) Melting points were taken on a microscope hot-stage calibrated against standard substances. Boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord in carbon tetrachloride solution in the region 2.5–7.0 μ , and in carbon disulfide solution in the region 7.0–15.0 μ . Solid analytical samples were dried *in vacuo* at 80° or at temperatures 30° below their melting points, whichever was lower. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(15) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(16) Cf. A. W. Johnson, "The Chemistry of the Acetylenic Compounds, Vol. I, The Acetylenic Alcohols," Edward Arnold Co., London, 1946, pp. 6–8.

(17) E. R. Coburn in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 696.

(18) F. H. Stross, J. M. Monger and H. deV. Finch, *THIS JOURNAL*, **69**, 1627 (1947).

(11) Kindly supplied by Dr. Kenneth W. Greenlee from the American Petroleum Institute Project No. 45 at the Ohio State University, Columbus, O.

(12) Cf. W. F. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *THIS JOURNAL*, **80**, 2384 (1958); see also B. S. Rabinovitch and K. W. Michel, *ibid.*, **81**, 5065 (1959).

(13) In a very recent paper all-*trans* 2,2-dimethyl-4-heptenal has been reported to result from the *in situ* generation and Claisen rearrangement of the vinyl ether derived from 1-penten-3-ol and isobutyraldehyde [K. C. Brannock, *THIS JOURNAL*, **81**, 3379 (1959)]. In this case, however, since *p*-toluenesulfonic acid was present as a catalyst throughout the 30-hour reaction period, there is perhaps some question whether any *cis* isomer would have survived, even if it were to have been formed in the rearrangement step. The stability of a *cis*-olefin under these reaction conditions was not determined.

The infrared spectra of these preparations showed typical strong vinyl ether absorption at 6.15, 6.25 and 8.4 μ ,¹⁰ as well as the features characteristic of the substituted allylic double bond noted above for the alcohols.

trans-4-Hexenals.—Rearrangement of the above purified vinyl ethers to the corresponding 3-substituted-*trans*-4-hexenals, VI, IX and XI, was conducted with samples ranging from 1 to 10 g. contained in sealed tubes fully immersed in the heating bath. The reaction appeared to proceed best at 170–180° (least amount of darkening) and was found to be essentially complete after 15–20 min. (disappearance of the vinyl ether peaks in the infrared spectrum). The products were obtained in 80–90% yield, after purification by distillation, and had the properties

trans-4-Hexenal	B.p., °C.		<i>n</i> _D ²⁰	Carbon, %		Hydrogen, %	
	°C.	mm.		Calcd.	Found	Calcd.	Found
VI ^a	136–137	745	1.4235	74.95	75.11	10.78	10.97
IX	59–61	25	1.4289	76.14	76.32	11.18	11.05
XI	79–81	23	1.4401	77.09	77.24	11.50	11.61

^a Product identical from the rearrangement of V or VII.

The infrared spectra of these unsaturated aldehydes had characteristic aldehyde absorption peaks at 3.7 and 5.8 μ ; in addition, each had a strong band at 10.3 μ , attributable to a *trans* disubstituted olefinic linkage.¹⁰ The 13–15 μ *cis* region was transparent. Gas chromatographic analysis of the once-distilled aldehydes on a Perkin-Elmer model 154 Vapor Fractometer ("C" column), and also on a Beckman GC-2 instrument (silicon—firebrick column) known to resolve comparable olefinic isomers effectively, indicated that each of the three aldehydes was essentially homogeneous. A mole-purity of at least 90% was indicated for the products as obtained directly from the rearrangement reaction.

The semicarbazone and 2,4-dinitrophenylhydrazone derivatives of these aldehydes were readily obtained in solid form and were recrystallized from ethanol or ethanol-water. Their melting points and analyses were

trans-4-Hexenal	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Semicarbazones							
VI	85–86	56.78	56.88	8.94	9.18	24.83	24.84
IX	133–134	58.98	59.13	9.35	9.36	22.93	23.08
XI	76–78	60.88	61.08	9.71	9.79	21.30	21.48
2,4-Dinitrophenylhydrazones							
VI	94–95	53.42	53.69	5.52	5.76	19.17	19.35
IX	100–101	54.89	55.08	5.92	6.02	18.29	18.30
XI	91–92	56.24	56.40	6.29	6.44	17.49	17.70

Interruption of the rearrangement of the *cis*-vinyl ethers V and X after 10–15 min. at 150–155°, or after 3–4 min. at 170–175°, furnished mixtures consisting of what appeared by infrared analysis to be about 80% aldehyde and 20% recovered vinyl ether. Fractional distillation of these mixtures over sodium at reduced pressure afforded recovered vinyl ethers whose boiling points, refractive indices and infrared spectra were substantially the same as those of the original samples. In neither case was there evidence for the presence of the corresponding *trans* isomer.

3-Substituted-hexenals.—Low-pressure catalytic hydrogenation of the preceding hexenals over 10% palladium-on-charcoal in ethanol solution at 25° afforded, in 90 to 95% yield after distillation, the corresponding 3-substituted hexanals, which had the properties

Hexenal	B.p., °C. (745 mm.)	<i>n</i> _D ²⁰
3-Methyl-	140–142	1.4098
3,3-Dimethyl-	142–144	1.4162
3-Propyl-	180–183	1.4277

^a Lit.¹⁹ b.p. 142–143° (755 mm.), *n*_D²⁰ 1.4122.

The semicarbazones and 2,4-dinitrophenylhydrazones of these saturated aldehydes readily deposited in crystalline form and were conveniently purified by recrystallization from ethanol or ethanol-water. Their melting points and analyses were

Hexenal	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Semicarbazones							
3-Methyl-3,3-Di-	107–109 ^a	56.11	56.23	10.01	9.95	24.54	24.39
methyl-	116–117	58.34	58.20	10.34	10.20	22.68	22.47
3-Propyl-	111–112	60.26	60.43	10.62	10.62	21.08	20.89
2,4-Dinitrophenylhydrazones							
3-Methyl-3,3-Di-	90–91	53.05	53.08	6.16	6.38	19.04	19.36
methyl-	98–99	54.53	54.83	6.54	6.80	18.17	18.34
3-Propyl-	69–70	55.88	56.16	6.88	6.96	17.38	17.60

^a Lit.¹⁹ m.p. 108–109° (no analysis reported).

3-Methyl- and 3,3-Dimethyl-trans-4-hexenoic Acids. Overnight oxidation of 4.0 g. of VI by the action of silver oxide (prepared from 12.0 g. of silver nitrate) in ethanol-water at 55–60° and pH 10 furnished, after isolation by acidification and extraction with ether, 2.5 g. (55% yield) of distilled 3-methyl-*trans*-4-hexenoic acid, b.p. 125–128° (25 mm.), *n*_D²⁰ 1.4327 [lit.²⁰ b.p. 209–210° (760 mm.?)]. Similarly, 4.0 g. of IX afforded 2.3 g. (51% yield) of 3,3-dimethyl-*trans*-4-hexenoic acid, b.p. 129–131° (25 mm.), *n*_D²⁰ 1.4383. This substance was characterized as its S-benzylthiuronium salt, which crystallized from absolute ethanol as small plates, m.p. 133–134°.

Anal. Calcd. for C₁₆H₂₄N₂O₂S (308.5): C, 62.29; H, 7.84; N, 9.08. Found: C, 62.00; H, 7.99; N, 8.98.

3-Methyl- and 3,3-Dimethylhexanoic Acids.—Catalytic hydrogenation of the above acids over palladium-in-ethanol furnished, respectively, 3-methylhexanoic acid, b.p. 212–215° (745 mm.), (lit.²¹ 215–216°), *n*_D²⁰ 1.4203, and 3,3-dimethylhexanoic acid, b.p. 218–220° (750 mm.), *n*_D²⁰ 1.4260. The latter was characterized as its S-benzylthiuronium salt, which deposited from ethanol as glistening plates, m.p. 147–148°.

Anal. Calcd. for C₁₆H₂₆N₂O₂S (310.5): C, 61.90; H, 8.44; N, 9.03. Found: C, 61.94; H, 8.48; N, 8.90.

(±)-trans-2-(α,γ-Dimethylallyl)-phenol (IIb).—(±)-*trans*-α,γ-Dimethylallyl phenyl ether (I) was prepared by the procedure of Alexander and Klüber² for the optically active material as modified by Goering and Jacobson.⁶ It had b.p. 52–54° (0.05 mm.), *n*_D²⁰ 1.5076 (lit.⁶ b.p. 59.8–60.0° (0.4 mm.), *n*_D²⁰ 1.5060). Its infrared spectrum contained a very intense absorption band at 10.3 μ attributable to a *trans* disubstituted double bond.¹⁰ Rearrangement of a 3.5-g. sample of this substance in a sealed tube at 195–200° for 1 hr. furnished, after separation of neutral material by extraction,² 2.1 g. of phenolic product with b.p. 65–80° (0.05 mm.). Fractional redistillation afforded 0.9 g. of product with b.p. 71–74° (0.05 mm.), *n*_D²⁰ 1.5318. These constants are in good agreement with those reported² for (+)-(α,γ-dimethylallyl)-phenol (II): b.p. 87° (0.3 mm.), *n*_D²⁰ 1.5360. The infrared spectrum also displayed the strong 10.3 μ absorption of the starting material; the 13–15 μ region was nearly transparent save for bands at 13.4 and 14.5 μ which were likewise present in the starting material.

***cis*-Olefin Stability Studies.**—A.P.I.¹¹ samples of 4-methyl-*cis*-2-pentene (XII) and 4,4-dimethyl-*cis*-2-pentene (XIII) (assayed¹¹ at 99.5+ % purity) were heated at 180 to 200° for periods up to 2 hr. in batches of 100 to 200 mg. contained in sealed glass ampoules fully immersed in the heating bath. The recovered olefins were unchanged in b.p. and infrared spectra (no decrease in the 14 μ *cis*-olefin band;¹⁰ no increase in the slight 10.4 μ *trans*-olefin peak¹⁰ present in the original samples). Samples of the corresponding *trans*-olefins (99+ % purity¹¹) were similarly treated and were also recovered without having undergone detectable alteration. Repetition of these experiments at 195 to 210° for 1 hr. with the addition of a molar equivalent of phenol likewise led to no detectable change in the infrared spectra of the recovered olefins.

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(19) A. Dewael and A. Weckering, *Bull. soc. chim. Belg.*, **33**, 495 (1924).

(20) H. v. Pechmann, *Ber.*, **33**, 3323 (1900).

(21) G. Ciamician and P. Silber, *ibid.*, **46**, 3077 (1913).

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Benylation of Arenes¹

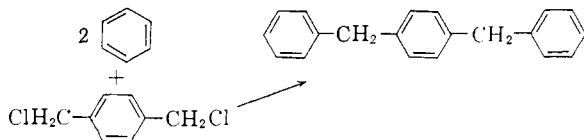
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Because diphenylmethanes unexpectedly resulted from reaction of α, α' -dichloro-*p*-xylene with arenes over aluminum amalgam, a study was made of such benzylation reactions with Friedel-Crafts catalysts. Ferric and antimony chlorides gave the expected products, but aluminum chloride—like aluminum amalgam—gave mainly diphenylmethanes. With the two sets of catalysts, benzyl chlorides also gave different products. Aluminum amalgam appears to function by the steady formation of small amounts of aluminum chloride. Benzylation reactions are apparently less unequivocal than heretofore supposed.

Introduction

A simple synthesis of dibenzylbenzenes would be condensation of arenes with α, α' -dichloro-*p*-xylene in the presence of Friedel-Crafts catalysts

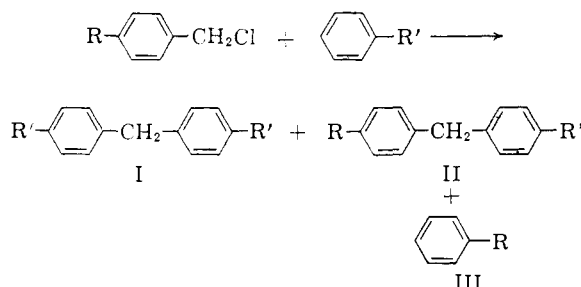


Aluminum amalgam has been used in benzyl chloride condensations, but when we tried it in this reaction we obtained diphenylmethanes rather than the expected dibenzylbenzenes. Aluminum amalgam had been selected because it is reported to cause fewer side reactions than aluminum chloride.²⁻⁸

We therefore investigated the benzylation reaction with various arenes. Benzene, chlorobenzene, toluene and *p*-xylene were benzylated with six different benzyl chlorides. Aluminum amalgam and chlorides of aluminum, iron and antimony were used as catalysts. To clarify a possible explanation of the observed results, diphenylmethanes were debenzylated over aluminum chloride.

Discussion

Table I summarizes the results of 13 benzylation experiments with aluminum amalgam and aluminum chloride. With either catalyst, benzyl chlorides in a 10 to 20 mole excess of arenes gave mainly diphenylmethanes of structure I, with only small amounts of the expected products, II. Arenes III, obtained in approximately equimolar amounts with I, formed by loss of the chloromethyl group from the benzyl chloride. Benzylation with α, α' -dichloro-*p*-xylene and aluminum amalgam or



aluminum chloride gave mostly diphenylmethanes. Dibenzylbenzenes constituted only one-tenth to one-fourth of the total product.

Our observations during the course of these reactions and the identity of the products from benzylation with either catalyst lead us to believe that aluminum amalgam functions through the formation of aluminum chloride. Aluminum amalgam has been reported to cause fewer side reactions than aluminum chloride. Aluminum amalgam may operate more efficiently because it produces aluminum chloride at a built-in controlled rate. As small amounts of aluminum chloride are destroyed by moisture or tied up in inactive complexes, additional fresh aluminum chloride is provided by the amalgam.

Table II lists the results of 9 benzylation catalyzed by ferric chloride and antimony pentachloride. Only the expected products were obtained. α, α' -Dichloro-*p*-xylene gave dibenzylbenzenes in 35 to 47% yields; benzyl chlorides gave the diphenylmethanes (II) in 44 to 85% yields.

We believe that in benzylation reactions catalyzed by aluminum chloride, the expected benzylation product is formed first and then undergoes transalkylation (debenzylation and rebenzylation) with the arene solvent to yield the observed products. A mixture of benzene, chlorodiphenylmethane and aluminum chloride was treated with hydrogen chloride gas under conditions similar to those employed for the benzylation reactions. The products were chlorobenzene and diphenylmethane. Thus, aluminum chloride can readily debenzylate diphenylmethanes.

Further support for transalkylation was obtained from the results of runs in which the mole

(1) Presented at the 136th A.C.S. Meeting, Atlantic City, N. J., 1959.

(2) W. W. Hartman and R. Phillips, "Organic Syntheses," Coll. Vol. II, edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 232.

(3) C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 1.

(4) H. R. Hirst and J. B. Cohen, *J. Chem. Soc.*, **67**, 826 (1895).

(5) R. Adams and K. R. Eilar, *THIS JOURNAL*, **73**, 1149 (1951).

(6) H. C. Brown and W. Grayson, *ibid.*, **75**, 6285 (1953).

(7) L. I. Diuguid, *ibid.*, **63**, 3527 (1941).

(8) F. Reindel and F. Seigel, *Ber.*, **56**, 1550 (1923).