that of the benzoyl derivative shows the same shift, masked partly, however, by additional absorption due to the benzoyl group.

We conclude, therefore, that, as in the case of isocarbostyril,[4] acylation of 3,4-dihydro-4-oxobenzo-1,2,3-triazine (I, R = H) yields the *N*-acyl derivatives (I, R = COMe, COPh), as originally suggested by Heller.

Experimental

Ultraviolet absorption spectra were determined for ethanol solutions (Higler Unicam spectrophotometer); infrared spectra were measured for Nujol and hexachlorobutadiene mulls (Perkin-Elmer 21 spectrophotometer). Compounds were prepared by Heller's methods; experimental details are given below in cases where his information is incomplete.

3,4-Dihydro-4-oxobenzo-1,2,3-triazine occurred as needles (from ethanol), m.p. 210° dec. (Heller, m.p. 213° dec.), ν_{max} 3140 (N—H) and 1695 cm.$^{-1}$ (C:O), λ_{max} 209 (ϵ 17,100), 225 (ϵ 20,050) and 281 mμ(ϵ 6100), λ_{min} 212 (ϵ 16,670) and 257 mμ (ϵ 3600), λ_{infl} 294 (ϵ 4300) and 305 mμ (ϵ 2750).

3-Acetyl-3,4-dihydro-4-oxobenzo-1,2,3-triazine.—Silver acetate (1.2 g.), dissolved in aqueous ethanol, was added with shaking to the triazine (1.1 g.) in warm ethanol. The silver salt separated as a white solid, was collected, and dried *in vacuo*.

Freshly distilled acetyl chloride (1 ml.) was added to a suspension of the silver salt (1.5 g.) in dry benzene (30 ml.), and the mixture was refluxed for 30 min. After standing overnight at room temperature, the silver chloride was removed, and the filtrate evaporated. The residual orange sirup slowly solidified. The acetyl derivative (0.7 g.) was crystallized from water, dried, and recrystallized from light petroleum (b.p. 100–120°), forming needles, m.p. 165° (Heller, m.p. 165°), ν_{max} 1695 and 1655 cm.$^{-1}$ (C:O) [*cf.* *N*-acetylisocarbostyril,[4] ν_{max} 1705 and 1665 cm.$^{-1}$], λ_{max} 219 (ϵ 23,100), 252 (ϵ 11,360) and 298 mμ (ϵ 4320), λ_{min} 239 (ϵ 9900) and 272 mμ (ϵ 3580), and λ_{infl} 261 mμ (ϵ 8400).

3-Benzoyl-3,4-dihydro-4-oxobenzo-1,2,3-triazine.—The triazine (1.5 g.) in warm ethanol was treated with sodium ethoxide (from 0.24 g. of sodium) in ethanol (30 ml.). After standing overnight at room temperature, ethanol was removed *in vacuo;* trituration of the residue with dry toluene gave the sodium salt (1.8 g.) as a white solid. This was converted to the benzoyl derivative (1 g.), which separated from light petroleum (b.p. 100–120°) as needles, m.p. 132° (Heller, m.p. 132–133°), ν_{max} 1718 and 1690 cm.$^{-1}$ (C:O), λ_{max} 209 (ϵ 26,150) and 227 mμ (ϵ 28,800), λ_{min} 213 mμ (ϵ 24,900), λ_{infl} 249 (ϵ 14,800) and 276 mμ (ϵ 9850).

Equilibration of *cis*- and *trans*-α-Methylstilbene in Presence of Potassium *t*-Butoxide as Catalyst[1]

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Incidental to the study of base-catalyzed reactions of alkenyl-benzenes *cis*- and *trans*-α-methylstilbenes have been equilibrated in the presence of catalytic amounts of potassium *t*-butoxide at 139 ± 1° and 200 ± 1°. The equilibrium mixture consisted, respectively, of 21.0% and 21.2% *cis*-, 76.8 and 74.0% *trans*-α-methylstilbene, and 2.2 and 4.8% 2,3-diphenyl-1-propene.

Cis- and *trans*-α-methylstilbene were synthesized by a modification of the procedure described by Abd Elhafez and Cram[3]. A mixture of the two diastereomers of 1,2-diphenyl-1-propanol was transformed to a solid mixture of two diastereomeric chlorides by the action of thionyl chloride in the presence of pyridine. The chlorides were separated into distinct diastereomeric species by fractional crystallization and subsequently dehydrohalogenated by means of 5% ethanolic potassium hydroxide[4] to give pure *cis*- and *trans*-α-methylstilbenes. Attempted preparation of pure *cis*-α-methylstilbene by the method described by Simamura and Suzuki[5] failed although the *trans* isomer was obtained in pure form. The equilibration reactions were made by refluxing a solution of methylstilbenes in either xylene or decahydronaphtalene in the presence of 0.1 *M* equivalent of potassium *t*-butoxide, based on the stilbenes used.

Starting with *trans* isomer in xylene solution (temp. 139 ± 1°), the equilibrium was reached after twenty-four hours while at 200°, in decahydronaphtalene solution, within one hour equilibrium was achieved. The progress of the reaction was investigated by taking out samples during the reaction and analyzing by gas chromatography. Equilibration reactions were also made using either pure *cis*-α-methylstilbene or a mixture of methylstilbenes enriched in the *cis* isomer.

It was found that 2,3-diphenyl-1-propene was formed in equilibrium concentration shortly after the reflux temperature of the solvent was reached; the double bond migration was much faster than the *cis-trans* isomerization. The composition of 1,2-diphenylpropenes at equilibrium is summarized in Table I. The hydrogenation of the equilibrated mixture produced only 1,2-diphenylpropane, which shows that the compounds present had the same skeleton as the starting α-methylstilbene.

TABLE I

EQUILIBRIUM MIXTURE OF *cis*- AND *trans*-α-METHYLSTILBENE AND 2,3-DIPHENYL-1-PROPENE

Temperature (±1°)	139°	200°
cis-α-Methylstilbene, %	21.0	21.2
trans-α-Methylstilbene, %	76.6	74.0
2,3-Diphenyl-1-propene, %	2.4	4.8

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(1) Paper XXIV of the series Base Catalyzed Reaction. For paper XXIII, see J. Shabtai, E. M. Lewicki, and H. Pines, *J. Org. Chem.*, **27**, 2618 (1962).

(2) On leave of absence from Polytechnic Institute, Lodz, Poland.

(3) F. A. Abd Elhafez and D. J. Cram, *J. Am. Chem. Soc.*, **75**, 340 (1953).

(4) E. Ellingboe and R. C. Fuson, *ibid.*, **55**, 2960 (1933).

(5) O. Simamura and H. Suzuki, *Bull. Chem. Soc. Japan*, **27**, 234 (1954).

The structure of 2,3-diphenyl-1-propene was established by means of ozonolysis. Formaldehyde and desoxybenzoin obtained from the ozonolysis by the reductive decomposition of the ozonide afforded final evidence of the position of the double bond in 2,3-diphenyl-1-propene.

The retention volumes of the diphenylpropenes and of some related compounds are summarized in Table II.

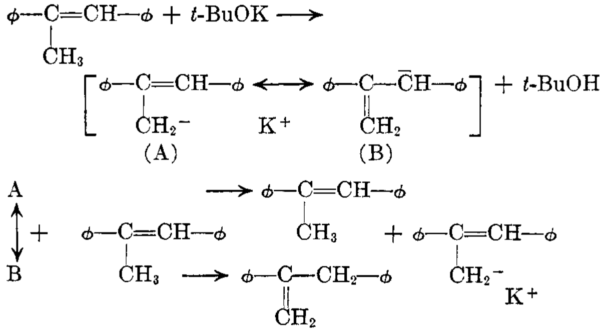
TABLE II

RETENTION VOLUMES TO α-METHYLSTILBENES AND OF RELATED COMPOUNDS RELATIVE TO PHENYLCYCLOHEXANE[a]

Compound	Rv/Rv Phenylcyclohexane Temp. 200°	Temp. 220°
cis-α-Methylstilbene	2.95	2.70
trans-α-Methylstilbene	5.35	4.65
2,3-Diphenyl-1-propene	3.44	3.14
1,2-Diphenylpropane	2.79	2.51
cis-1,2-Diphenylcyclopropane	3.68	3.33
trans-1,2-Diphenylcyclopropane	5.44	4.74

[a] 4 m. column filled with 8% silicon (Dow-Corning 550 fluid) on 30–60 mesh chromosorb P; helium flow rate, 75 ml./min.; helium pressure, 35 p.s.i.

The isomerization reaction most probably involves the removal of an allylic proton to form a carbanion and can be presented as follows:



The resonance structure (B) of the carbanion formed is more reactive than the form (A) because of smaller delocalization of the negative charge in the anion. For this reason it can metallate an α-methylstilbene molecule relatively fast, giving rise to the formation of 2,3-diphenyl-1-propene. The reaction explains the rapid appearance of this compound in the mixture. The rotation around the C—C bond in the carbanion (B) followed by its transformation to the form (A) and chain propagation reaction leads to relatively slow *cis-trans* isomerization.

Experimental

1,2-Diphenyl-1-propanol.—This compound was prepared from 100.5 g. (0.75 mole) of 2-phenylproponaldehyde, 21.1 g. (0.9 g.-atom) of magnesium, and 141.3 g. (0.9 mole) of bromobenzene.[6a] Anhydrous ether, 500 ml., was used as solvent. The addition product was decomposed with 400 ml. of cold 20% sulfuric acid, the organic layer was separated, dried over anhydrous magnesium sulfate, and distilled *in vacuo* yielding 79.5 g (50%) of colorless oil, b.p. 170–175°/9 mm. Hg; n^{25}_{D} 1.5707.

1,2-Diphenyl-1-propyl Chloride.—Thionyl chloride, 59.5 g. (0.5 mole), was added over a period of 30 min. to a stirred mixture of 79.5 g. (0.38 mole) of 1,2-diphenyl-1-propanol and 36.4 g. (0.4 mole) of pyridine placed in an ice bath. The resulting thick brown oil was stirred at room temperature for an additional 30 min. and then heated at 60–65° for 1 hr. and at 90–100° for 1.5 hr. until the evolution of sulfur dioxide ceased. The mixture was poured on 200 g. of ice. The reaction product solidified immediately. It was filtered, washed with cold water, and crystallized twice from 100 ml. and 60 ml. of ethanol. In order to resolve the mixture into pure *erythro* and *threo* chlorides, the crystals were extracted with five 100-ml. portions of hot *n*-pentane; the solution was cooled immediately. The insoluble residue and the first crop of crystals were found to be pure *dl-erythro*-chloride, colorless plates (after recrystallization from ethanol-benzene), m.p. 140–141° (reported m.p. 139.5–140.5°).[6b] Yield 10.0 g. (11%). From the mother liquor, 41.0 g. (48%) of *dl-threo*-chloride has been obtained in the form of colorless needles which after recrystallization from ethanol melted at 56.5–57° (reported 54–55°).[6b]

Anal. Calcd. for $C_{15}H_{15}Cl$: C, 78.08%; H. 6.55%. Found: *dl-Threo*-isomer, C, 78.27%: H, 6.43%. *dl-Erythro*-isomer, C, 78.44%; H, 6.34%.

***cis*-α-Methylstilbene.**—*dl-erythro*-1,2-Diphenyl-1-propyl chloride, 5.8 g. (0.025 mole) in 250 ml. of 5% ethanolic potassium hydroxide solution was refluxed for 16 hr. The solvent was then removed *in vacuo*, and the residue washed with cold water. The crude *cis*-α-methylstilbene was recrystallized from 10 ml. of hot methanol. Colorless prisms were obtained melting at 49–50° (reported m.p. 47–48°[6a]), yield, 4.4 g. (90%)

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74%; H, 7.26%. Found: C, 92.33%; H, 6.96%.

***trans*-α-Methylstilbene.**—*dl-threo*-1,2-Diphenyl-1-propyl chloride, 5.8 g. (0.025 mole), was dehydrohalogenated as described above. Yield, 4.5 g. (93%). The *trans*-α-methylstilbene in the form of colorless plates (from ethanol) melted at 82–83°.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74%; H, 7.26%. Found: C, 92.90%; H, 7.32%.

Equilibration of *cis*- and *trans*-α-Methylstilbenes. General Procedure.—A 1.94-g. sample (0.01 mole) of α-methylstilbene was refluxed in 20.0 g. of the suitable solvent in presence of 0.11 g. (0.001 mole) of potassium *t*-butoxide. Samples were taken periodically and analyzed by gas chromatography.

Hydrogenation of the Equilibrated Mixture.—An equilibrated mixture of diphenylpropenes at 200°, 1.94 g., was hydrogenated at room temperature and at atmospheric pressure in the presence of 0.2 g. of 5% palladium on charcoal. The hydrogenated product was found to be pure 1,2-diphenylpropane.

Ozonolysis.—An equilibrated mixture of diphenylpropenes at 139°, 9.7 g. (0.05 mole) in 50 ml. of carbon tetrachloride was ozonized at −20°. The ozonide was decomposed by refluxing the solution for 2 hr. in the presence of 20 ml. of acetic acid and 20 g. of zinc powder. The gases evolved were passed through a solution of 0.5 g. of dimedone in 25 ml. of water and 10 ml. of ethanol. The solid obtained, 0.2 g., after recrystallization from ethanol melted at 187–188° and did not depress the melting point of an authentic sample produced from the condensation of formaldehyde with dimedone.

The solution obtained after the decomposition of the ozonide was found to consist according to gas chromatographic analysis, of benzaldehyde, acetophenone, and desoxybenzoin.

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(6) D. J. Cram and F. A. Abd Elhafez (a) *J. Am. Chem. Soc.*, **74**, 5828 (1952); (b) *ibid.*, **74**, 5851 (1952).