cracking pattern) and nmr (expected signals in the proper ratio) spectra. Benzylic hydrogen (nmr signal at *ca.* δ 2.7) was clearly present in the triethylaluminum–benzotrichloride reaction mixture before hydrolysis. Hydrolysis with deuterium oxide did not lead to detectable (mass analysis) deuteration of the 3-phenylpentane. Use of hydride-free triethylaluminum (distilled from 1-octadecene) did not significantly alter the product composition. When the ether and the alkylaluminum in the reaction mixture were equimolar, the benzylic halide reactions were incomplete.

The neophyl chloride–triethylaluminum reaction was also rapid (but less vigorous than the benzylic halide reactions) at 10°. Isobutyl benzene (doublet nmr signal in the benzylic H region) was present in the reaction mixture before hydrolysis. The gas evolved before hydrolysis contained 30% ethane and 64% ethylene (7.6 and 17% yield, respectively, based on neophyl chloride). Reaction of neophyl chloride with a mixture of 2 molar equiv each of triethylaluminum and diethylaluminum hydride, and 1 equiv of butyl ether gave 2,2-dimethyl-1-phenylbutane and isobutylbenzene in 42 and 36% yield, respectively.

Propargyl Chloride and Tributylaluminum.—Addition of propargyl chloride (5.0 g, 68 mmoles) to a solution of tributylaluminum (17 ml, 70 mmoles) in 30 ml of xylene caused no indication of immediate reaction. After 2 days at 25°, the mixture was hydrolyzed by adding cautiously to dilute hydrochloric acid. Distillation of the neutralized organic layer gave 4.4 g of product boiling principally at 96–101°. The product contained 88% 1,2-heptadiene (3.9 g, 40 mmoles, 59%), identified by mass and nmr spectra and by comparison of its infrared spectrum with a published spectrum.[45] At most, a trace of 1-heptyne was present. 1-Heptene (1.5% yield) accompanied the heptadiene.

(45) J. H. Wotiz, *J. Am. Chem. Soc.*, **73**, 693 (1951). The spectrum was compared with the spectrum of the 103° boiling product in Figure 1.

Triethylaluminum and triisobutylaluminum reacted similarly with propargyl chloride. A larger scale reaction with triethylaluminum gave a pronounced exotherm. Although propargyl chloride and diethylaluminum chloride reacted slowly at 25° to give a dark brown mixture, no 1,2-pentadiene was detectable among the products (these and the following results were obtained with nmr analysis). Propargyl chloride and triethylaluminum in cyclohexene or styrene gave the usual yields of 1,2-pentadiene. Triethylaluminum and diethylaluminum chloride reacted slowly with 1-pentyne; however, no 1,2-pentadiene was formed.

1-Chlorooctane and Triethylaluminum.—After 18 days at 100°, a mixture of 1-chlorooctane (5.2 g, 35 mmoles), triethylaluminum (15 ml, 110 mmoles), and ethyl ether (2.7 g, 36 mmoles) in 50 ml of hexane was treated with additional ether (15 ml) and hydrolyzed with 20% sodium hydroxide. The organic hydrolysate was analyzed, and the constituents (1.4% unreacted 1-chlorooctane, decane, 3-methylnonane, octenes, and octane) were identified by vpc. 3-Methylnonane was identified by comparison with the product prepared from 2-chlorooctane.

2-Chlorooctane and 3-chloro-3-methylheptane reacted with triethylaluminum at lower temperatures than did 1-chlorooctane; otherwise, the same procedure was used. The product mixtures obtained from 1- and 2-chlorooctane in the absence of ether were similar to the mixtures obtained with ether.

Acknowledgment.—The author is grateful to the Analytical Section of Continental Oil Company for the fine support accorded this work, and in particular to Dr. P. W. Flanagan for nmr analyses, Mr. M. C. Hamming for mass analyses, and Mr. E. E. Smith for many vpc separations. The valuable technical assistance of Messrs. G. C. Neidig, L. Rose, and H. J. Powell is also acknowledged.

Tropyl as a Migrating Group. I. The Acetolysis of 2-Tropyl-2-phenylethyl *p*-Toluenesulfonate

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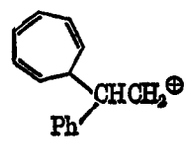
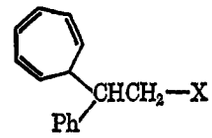
2-Tropyl-2-phenylethyl *p*-toluenesulfonate (IIc) has been prepared from 2-tropyl-2-phenylethanol, obtained in turn by reduction of 2-tropyl-2-phenylacetic acid. The latter acid was prepared by the alkylation of phenylmalonic acid with tropylium bromide in pyridine. Acetolysis of tosylate IIc in refluxing acetic acid yielded a hydrocarbon fraction containing 15% *cis*- and 85% *trans*-1,3-diphenylpropene (III) and an acetate fraction containing seven as yet uncharacterized components. A mechanism is proposed for the ring contraction involved in the transformation IIc → III.

To the best of our knowledge, the 1,3,5-cycloheptatrien-7-yl (tropyl) group has never been observed as a stable migrating entity in cationic 1,2 shifts. Furthermore, recent reviews of the chemistry of cycloheptatriene and its numerous derivatives[3] fail to record experiments specifically designed to examine the possibility that the tropyl group may act as a 1,2 migrant, or—if so—to establish its relative migratory aptitude. Our interest in molecular rearrangements has prompted us to examine this problem, and our preliminary observations are reported herewith.

Our initial efforts have involved attempts to generate the 2-tropyl-2-phenylethyl carbonium ion (I) during dehydration of the alcohol IIa, deamination of the amine IIb, and solvolysis of the tosylate IIc. Degradative examination of the olefinic or oxygenated products from IIa, IIb, or IIc (appropriately labeled



I



IIa, X = OH
b, X = NH_2
c, X = OTs

with carbon-14 at C-1 or C-2) would then allow evaluation of the relative extents to which phenyl or tropyl had migrated in I prior to its irreversible product-forming step. This simple labeling technique has been successfully utilized to establish relative migra-

(1) National Science Foundation Science Teaching Faculty Fellow, 1962–1963.

(2) National Science Foundation Science Teaching Faculty Fellow, 1960–1961.

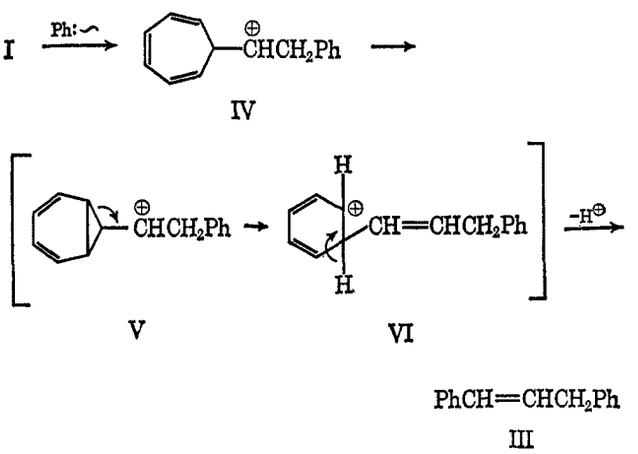
(3) (a) T. Nozoe in "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter VII; (b) A. Heusner, *Angew. Chem.*, **70**, 693 (1958); (c) W. von E. Doering and H. Krauch, *ibid.*, **68**, 661 (1956); (d) P. L. Pauson, *Chem. Rev.*, **55**, 9 (1955); (e) W. Baker and J. F. W. McOmie, *Progr. Org. Chem.*, **3**, 62 (1955); (f) A. W. Johnson, *J. Chem. Soc.*, 1331 (1954); (g) J. W. Cook and J. D. Loudon, *Quart. Rev.* (London), **5**, 99 (1951).

tory aptitudes in similar reactions involving a series of 2-phenyl-2-arylethanols,[4] 2-phenyl-2-arylethylamines,[5] and 2-phenyl-2-arylethyl tosylates.[6] Dehydration experiments with IIa and nitrous acid deamination experiments with crude IIb led initially only to tarry or polymeric materials and were accordingly abandoned. The acetolysis of 2-tropyl-2-phenylethyl *p*-toluenesulfonate (IIc) in refluxing acetic acid, however, led to cleaner product mixtures and was examined therefore in greater detail.

The desired tosylate IIc was conveniently prepared (unlabeled) by the following sequence of reactions. Methyl tropylphenylmalonate (mp 62–64°) or ethyl tropylphenylmalonate (oil) were readily obtained by reaction of tropylium bromide[7] with the corresponding phenylmalonic ester in warm pyridine solution. Hydrolysis of the former esters followed by spontaneous decarboxylation yielded tropylphenylacetic acid, mp 119–120°, which could also be prepared directly by reaction of phenylmalonic acid with tropylium bromide in warm pyridine. Reduction of the above tropylphenylacetic acid with lithium aluminum hydride in tetrahydrofuran afforded 2-tropyl-2-phenylethanol (IIa, mp 70–71°), which was readily converted to the tosylate IIc (mp 88–91°) on reaction with *p*-toluenesulfonyl chloride in pyridine. In the course of these studies methyl tropylphenylacetate (mp 63.5–67°), tropylphenylacetamide (mp 164.5–165.5°), α-tropylacetophenone (semicarbazone mp 192–193.5°, 2,4-dinitrophenylhydrazone mp 182°), 1-phenyl-2-tropylethanol (mp 48.5–50°), and 2,3-diphenyl-1-propyl *p*-toluenesulfonate (mp 75–76°) were also prepared. Catalytic reduction of the above tosylate IIc using 30% Pd–C resulted in the uptake of 3 molecular equiv of hydrogen, a result also obtained on similar reduction of the above tropylphenylacetic acid.

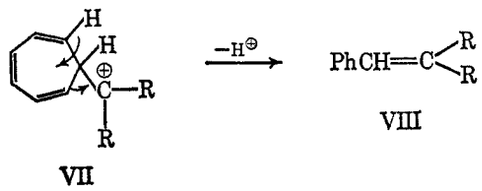
When the above 2-tropyl-2-phenylethyl *p*-toluenesulfonate (IIc) was heated for 9.5 hr in refluxing acetic acid containing sodium acetate and then processed for products, a brown oil was obtained. This was separated chromatographically into a hydrocarbon fraction and an ester (acetate) fraction. Vapor phase chromatography and product isolation from the hydrocarbon fraction showed it to consist of a 15:85 mixture of *cis*- and *trans*-1,3-diphenylpropene (III), olefins whose configurations we have recently established.[8,9] Vapor phase chromatographic examination of the above ester fraction revealed the presence of at least seven components. These have not been characterized as yet, but the major one of them had a vpc retention time identical with that of 2-tropyl-2-phenylethyl acetate. These ester products are presently under investigation.

Conversion of the 2-tropyl-2-phenylethyl carbonium ion (I) into 1,3-diphenylpropene during acetolysis of IIc clearly involves contraction and aromatization of the tropyl ring system. We rationalize this novel and unexpected observation by postulating an initial 1,2 migration of the phenyl group in I, yielding the



rearranged 1-tropyl-2-phenylethyl carbonium ion (IV). The latter may then suffer valence bond isomerization to the analogous norcardiene ion V, which in turn can shift its electrons (VI) and lose a proton to form the observed 1,3-diphenylpropene product (III). Although the transformation of IV into III may be formulated in an alternative way (see VII below), it is tempting to speculate on the actual transitory existence of the norcardiene intermediate V. Thus, while there is no evidence for norcaradiene structures in simple cycloheptatriene derivatives,[10–12] the presence of strongly electron-withdrawing groups on the tropilidene ring apparently favors the norcaradiene structure,[13] and such a structure is thus logical adjacent to a carbonium center. Furthermore, the transformation V → VI is analogous to the frequently observed conversion of the cyclopropylcarbinyl cation into allylcarbinyl derivatives.[14]

The contraction of the seven-membered ring of tropones, tropolones, and their derivatives, usually under alkaline conditions, to form benzenoid derivatives is a widely observed and well-documented phenomenon.[15] Similarly, tropylium salts,[7,16,17] tropylidene itself,[17] and carboxytropylidene[18] have been observed to yield benzene and benzene derivatives on oxidation with H_2O_2 or CrO_3, and mechanisms formally analogous to parts of that suggested above have been proposed[7,17] to rationalize such oxidative ring contractions. The most direct analogy to our present observation, however, appears in studies of Ganellin and Pettit, who report that carbonium ions of type VII rearrange spontaneously to substituted styrenes (VIII), the driving force being



(4) J. G. Burr, Jr., and L. S. Ciereszko, *J. Am. Chem. Soc.*, **74**, 5426 (1952).
(5) L. S. Ciereszko and J. G. Burr, Jr., *ibid.*, **74**, 5431 (1952).
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(7) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954); **79**, 352 (1957).
(8) E. K. Raunio and W. A. Bonner, *J. Org. Chem.*, **31**, 000 (1966).
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(10) F. R. Jensen and L. A. Smith, *J. Am. Chem. Soc.*, **86**, 956 (1964).
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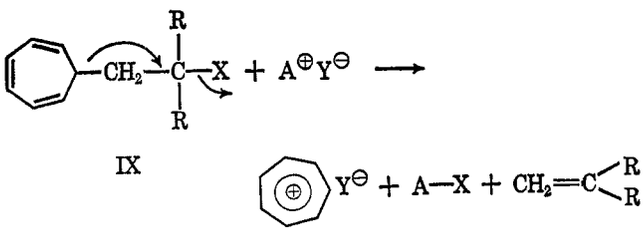
(13) E. Ciganek, *ibid.*, **87**, 652 (1965).
(14) R. Breslow in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 259 ff.
(15) *Cf.* ref 3d, p 75 ff, for a large number of specific examples.
(16) M. E. Volpin and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **126**, 780 (1959); *Chem. Abstr.*, **53**, 21850e (1959).
(17) G. Juppe and A. P. Wolf, *Chem Ber.*, **94**, 2328 (1961).
(18) M. J. S. Dewar, C. R. Ganellin, and R. Pettit, *J. Chem. Soc.*, 55 (1958).

the resonance energy of the aromatic ring.[19] Thus, Ganellin and Pettit found that 2-tropyl-2-propanol yields 1-phenyl-2-methyl-1-propene on dehydration with alcoholic hydrogen chloride and that tropyl methyl ketone affords benzyl methyl ketone with the same reagents,[19] while Doering has observed that the action of acid on tropylmethanol yields styrene.[20] The essential intermediate in such transformations is a carbonium center adjacent to the tropyl ring system, an intermediate which is achieved in our mechanism only after the 1,2 shift of phenyl involved in the transformation I → IV.

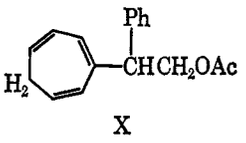
Conrow[21] has recently provided evidence for an alternative path by which β-tropylethyl derivatives may react, namely fragmentation. Thus, 1-tropyl-2-



IX

methyl-2-propanol, for example, yielded tropylium perchlorate and isobutylene on treatment with perchloric acid in acetonitrile. This process, to which tertiary alcohol and halides of type IX are particularly susceptible, has been suggested[21] to proceed by either a carbonium ion or a concerted mechanism. In our system and under our conditions, however, the carbonium ion I does not appear disposed to follow such a reaction path. An interesting formal "reversal" of our observed ring contraction has been observed by Nelson[22] and co-workers, who noted that the solvolysis of 1,4-dihydrobenzyl *p*-toluenesulfonate yielded 88% tropylidene and 12% toluene, a ring expansion which has more recently been developed into a more general synthesis of tropenoid compounds,[23] as well as the heptalene system.[24] Ring expansions from the benzyl to the tropyl system have also been observed on electron impact in the mass spectrometer.[25-27]

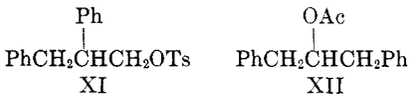
The plethora of acetate products which we have observed on solvolysis of our tosylate IIc is tentatively explainable in terms of thermal isomerization of the tropyl group in either the starting material or those acetate products which have an intact tropyl group. Thus Ter Borg and co-workers have found that both cycloheptatriene[28] and phenylcycloheptatriene[29] undergo thermal isomerization by successive transannular 1,5 hydrogen migrations which occur at relatively low temperatures (130–140°). Since our acetolysis was conducted in refluxing acetic acid (118°), it seems possible that double-bond isomers analogous



X

to X may comprise several of our observed acetate products. This supposition is currently under investigation.

As mentioned above, our postulated mechanism for the conversion of tosylate IIc into 1,3-diphenylpropene requires exclusive prior 1,2 migration of the phenyl group in the carbonium ion I. In support of this hypothesis is our observation that the acetolysis of 2,3-diphenyl-1-propyl *p*-toluenesulfonate (XI) leads



XI XII

again not only to 1,3-diphenylpropene but also to 1,3-diphenyl-2-propyl acetate (XII). The latter product, at least, must result from exclusive 1,2 migration of the C-2 phenyl group (as opposed to C-2 benzyl) in the initial primary carbonium ion from XI. While aryl groups show greater migratory aptitude than alkyl groups in general during Wagner–Meerwein 1,2 shifts, the superior migratory aptitude of certain alkyl groups over aryl groups in other 1,2 shifts (for example, in the Baeyer–Villiger[30-32] and related[33] reactions), however, places the postulate of *exclusive* phenyl 1,2 migration in carbonium ion I on perhaps less certain grounds. We have, therefore, initiated experiments using C^{14}-labeled analogs of tosylate IIc, whereby we hope the question of the migratory capability of the tropyl group may be resolved.

Experimental Section

Tropylium Bromide.—Freshly distilled tropilidene[34] (bp 114–115°) was converted to tropylium bromide according to the procedure of Doering and Knox.[7] The crude product was stored *in vacuo* over potassium hydroxide prior to use, and was employed without further purification.

Ethyl Tropylphenylmalonate.—A solution of ethyl phenylmalonate (9.4 g, 0.04 mole) and tropylium bromide (6.8 g, 0.04 mole) in pyridine (40 ml) was heated on the steam bath for 3 hr, cooled, and poured into 1.5 *N* sulfuric acid (330 ml). The mixture was extracted with ether, and the ether layer was washed with water, dried over magnesium sulfate, decolorized with Norit, and stripped of solvent to yield 11.4 g (87.4%) of crude ethyl tropylphenylmalonate, a brown oil. The product was stirred vigorously for several minutes with boiling 20% aqueous sodium hydroxide, then the mixture was cooled, diluted with water, and extracted with hexane. The extract was dried, decolorized, and stripped of solvent to yield 6.7 g of light yellow oil, homogeneous on thin layer chromatography and showing λ_{max}^{hexane} 258 mμ (ε 3890). Attempts to distil the sample evidenced decomposition.

Anal. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found: C, 73.08; H, 7.01.

Methyl Tropylphenylmalonate.—A mixture of methyl phenylmalonate (18.3 g, 0.088 mole), tropylium bromide (22 g, 0.13 mole), and pyridine (100 ml) was stirred overnight and then poured into a mixture of ice and hydrochloric acid. Thorough extraction with ether, followed by washing, drying, and solvent removal afforded 24.2 g of brown oil. This was dissolved in an

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(20) Private communication reported in ref 19.
(21) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).
(22) N. A. Nelson, F. H. Fassnacht, and J. U. Piper, *ibid.*, **81**, 5009 (1959); **83**, 206 (1961).
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(34) Obtained through the courtesy of Shell Chemical Corp., Emeryville, Calif.

equal volume of methanol and the solution was chilled, resulting in the crystallization of 18.4 g (70%) of crude product. Repeated recrystallization from methanol provided a sample having mp 62–64°.

Anal. Calcd for $C_{16}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.66; H, 6.25.

Tropylphenylacetic Acid.—A mixture of phenylmalonic acid (21.8 g, 0.12 mole) and tropylium bromide (20.7 g, 0.12 mole) in tetrahydrofuran (100 ml) was treated with pyridine (20 ml), then heated under reflux with stirring for 2.5 hr. Rapid carbon dioxide evolution commenced at the outset of heating and had ceased by the end of the reflux period. The cooled suspension was poured into water (900 ml) containing sodium hydroxide (10 g). The resulting solution was extracted with ether (discard), acidified with sulfuric acid, and reextracted well with ether. The extract was washed with saturated aqueous sodium chloride, treated with 5 ml of ethanol, and stripped of solvent by rotary vacuum evaporation at 100°, leaving 26 g of brown oil which crystallized on dilution with benzene (10 ml). The mixture was triturated with petroleum ether (bp 30–60°) and the crude tropylphenylacetic acid (16.0 g, 58.5%) was filtered: mp 116–119°. A sample purified by dissolving in benzene, filtering through a layer of silica gel, and recrystallizing from benzene–hexane had mp 119–120° and λ_{max}^{EtOH} 250 mμ (ε 3590).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; neut. equiv., 226. Found: C, 79.64; H, 6.38; neut. equiv., 224.

Hydrolysis followed by decarboxylation of the above samples of methyl and ethyl tropylphenylmalonates, using refluxing aqueous ethanol slutions of potassium hydroxide, likewise afforded samples of tropylphenylacetic acid having properties similar to that described above. Catalytic hydrogenation of such samples, using 30% Pd–C catalyst in ethanol, resulted in the uptake of 3 molecular equiv of hydrogen.

Methyl Tropylphenylacetate.—This product was obtained as a colorless solid by esterification of the above tropylphenylacetic acid with a slight excess of diazomethane in ether solution. Two recrystallizations from hexane afforded a sample having mp 63.5–67°, $\lambda_{max}^{cyclohexane}$ 258 mμ (ε 3680).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.83; H, 6.69.

Tropylphenylacetamide.—A stirred solution of ethyl phenylcyanoacetate (945 mg, 5 mmoles) in pyridine (5 ml) was treated with tropylium bromide (860 mg, 5 mmoles), resulting immediately in a white precipitate. The mixture was heated under reflux for 20 min, then cooled and poured into 1 *M* hydrochloric acid (50 ml), then was extracted with ether. Customary processing afforded 1.2 g (86%) of crude tropylphenylcyanoacetate as a dark yellow oil. An attempt was made to hydrolyze and decarboxylate this crude product directly to the above tropylphenylacetic acid by heating with potassium hydroxide (1.20 g) in refluxing methanol (3 ml) for 15 min, then adding water (2 ml) and heating for an additional 20 hr. While the odor of ammonia was evident during the above reaction, hydrolysis proved incomplete. On pouring the mixture into water, a solid formed, mp 160–162°. The material was recrystallized from benzene giving 150 mg, mp 164.5–165.5, which proved to be tropylphenylacetamide.

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.04; H, 6.90; N, 5.93.

A mixture of the above tropylphenylacetic acid (5 g) in benzene (25 ml) containing thionyl chloride was heated under reflux for 1.5 hr. Volatiles were removed under vacuum (20 mm) at 100°, the residual oil was dissolved in benzene (50 ml), and the solution was treated with a stream of gaseous ammonia for 15 min. Customary isolation and recrystallization from benzene yielded a total of 4.15 g (83.3%) of crude tropylphenylacetamide, mp 158–162°, mmp 158–162° with the above sample.

2-Tropyl-2-phenylethanol.—A solution of tropylphenylacetic acid (10.7 g) in tetrahydrofuran (75 ml) was added slowly to a stirred suspension of lithium aluminum hydride (2.6 g) in tetrahydrofuran (100 ml). The mixture was stirred for 0.5 hr at room temperature and under reflux for 2.5 hr, then was cooled and cautiously treated with water (15 ml) containing sodium hydroxide (1 g). The granular solid was filtered and the filtrate was stripped of solvent to yield 10.1 g (100%) of crude 2-tropyl-2-phenylethanol, a viscous tan oil which was homogeneous on thin layer chromatography and showed strong hydroxyl absorption at 3385 cm^{-1}. The product crystallized slowly on standing and was recrystallized several times from hexane and from aqueous methanol as colorless prisms, mp 70–71° (hot stage), $\lambda_{max}^{cyclohexane}$ 257–258 mμ (ε 3890).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.10; H, 7.74.

A similar product was obtained by reduction of the above methyl tropylphenylacetate with lithium aluminum hydride.

2-Tropyl-2-phenylethyl *p*-Toluenesulfonate.—To a cold stirred solution of 2-tropyl-2-phenylethanol (10.0 g, 0.047 mole) in pyridine (50 ml) was added in small portions 14.1 g (0.074 mole) of *p*-toluenesulfonyl chloride. The mixture was stirred at 0° for 1 hr and at room temperature for 1 hr, then was poured onto ice (400 g) mixed with sulfuric acid (20 ml). The crude crystalline product was collected and air dried, giving 18.5 g (107%), mp 75–89°. After several recrystallizations from benzene–hexane the sample had mp 88–91°, $\lambda_{max}^{cyclohexane}$ 257 mμ (ε 4010).

Anal. Calcd for $C_{22}H_{22}O_3S$: C, 72.10; H, 6.05. Found: C, 72.06; H, 6.00.

The above sample absorbed 3 molecular equiv of hydrogen on catalytic hydrogenation using 30% Pd–C in ethanol.

α-Tropylacetophenone.—Sodium (1.2 g, 0.052 g-atom) was converted to "sand" under boiling xylene, then suspended, after rinsing with tetrahydrofuran, in tetrahydrofuran (125 ml). Ethyl benzoylacetate (10.0 g, 0.052 mole) was added and the mixture was stirred overnight, whereupon the sodium dissolved. Tropylium bromide (9.0 g, 0.052 mole) was then added and the mixture was stirred under reflux for 60 min, then was cooled, and filtered, rinsing the cake (5.8 g) with ether. The combined filtrate and rinsings were stripped of solvent under vacuum. and the residue was dissolved in ethanol (50 ml) and filtered from a small amount of insoluble material. The filtrate was treated with a mixture of ethanol (170 ml), water (50 ml), and potassium hydroxide (5.5 g), allowed to stand at room temperature overnight, then was diluted with water (650 ml), saturated with sodium chloride, and extracted with ether until the extracts were colorless. The extracts were evaporated under vacuum and the residue was redissolved in ether. The solution was washed with water, treated with methanol (10 ml), and evaporated to dryness under vacuum at 100°, leaving 8.46 g (77.5%) of crude α-tropylacetophenone. Attempts to distil the product (1 mm) resulted in considerable decomposition. The crude material showed one main spot and one small spot in thin layer chromatography, with no evidence of unreacted starting material. The crude ketone was characterized as its semicarbazone and 2,4-dinitrophenylhydrazone. The former, recrystallized from methanol, consisted of thin plates, mp 192–193.5°.

Anal. Calcd for $C_{16}H_{17}NO_3$: C, 71.88; H, 6.41; N, 15.72. Found: C, 71.79; H, 6.40; N, 15.53.

The 2,4-dinitrophenylhydrazone was recrystallized from acetic acid, mp 182°.

Anal. Calcd for $C_{21}H_{18}N_4O_4$: C, 64.60; H, 4.65; N, 14.35. Found: C, 64.64; H, 4.68; N, 14.14.

1-Phenyl-2-tropylethanol.—A solution of the above α-tropylacetophenone (8.4 g) in absolute ether (50 ml) was added slowly to a stirred suspension of lithium aluminum hydride (1.9 g) in ether (100 ml). Stirring was continued for 2.5 hr, the excess hydride was destroyed by slowly adding aqueous sodium hydroxide (10%, 4 ml), and the reaction mixture was processed as usual, yielding 7.74 g (91.2%) of crude product, an amber oil. This was crystallized (Norit) by dissolving it in petroleum ether containing some benzene, chilling, and seeding. The product was recrystallized from hexane as fine, long needles, mp 48.5–50°.

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.94, 84.88; H, 7.66, 7.93.

2,3-Diphenyl-1-propyl *p*-Toluenesulfonate.—2,3-Diphenyl-1-propanol was prepared by the reduction of 2,3-diphenylpropanoic acid with lithium aluminum hydride in ether. The alcohol (2.5 g) was converted to its tosylate (3.76 g, 87%) by reaction with *p*-toluenesulfonyl chloride in pyridine as described above. After three recrystallizations from benzene–hexane, the product had mp 75–76°.

Anal. Calcd for $C_{22}H_{22}O_3S$: C, 72.10; H, 6.05. Found: C, 71.91; H, 6.32.

Acetolysis of 2-Tropyl-2-phenylethyl *p*-Toluenesulfonate.—A solution of the above 2-propyl-2-phenylethyl tosylate (5.0 g) and freshly fused sodium acetate (1.2 g) in glacial acetic acid (50 ml) was heated under reflux for 9.5 hr, then allowed to stand overnight, and stripped of solvent under vacuum at 100°. The brown residue was shaken with water (100 ml) and ether (50 ml), and the aqueous layer was reextracted twice with ether.

The ether extracts were washed with water, dilute sodium hydroxide solution, and water, then treated with methanol (10 ml), and evaporated to dryness under vacuum at 100°, leaving 2.92 g of brown liquid. This was dissolved in petroleum ether (bp 30–60°) and the solution was passed through a 1.8 × 9 cm column of silica gel G, eluting with petroleum ether until the dark brown band was about to emerge. Solvent removal from the eluate left 2.58 g of amber oil which was chromatographed again on a 1.8 × 25.5 cm column of silica gel G. Progress of the colorless fraction could be followed visually by change in the appearance of the absorbent, and elution of this material was accomplished using 100 ml of petroleum ether, collected in seven fractions. The first 5-ml fraction afforded 0.14 g of mobile colorless oil, and the remaining six fractions afforded 0.77 g. The column was further eluted with benzene (152 ml), from which eluate 1.20 g of viscous liquid resulted on evaporation.

Vapor phase chromatography (5-ft analytical column of 20% silicone rubber on 45–60 mesh firebrick, 200°) of the first fraction above showed two constituents. The leading fraction was isolated by preparative vapor phase chromatography, and proved to be *cis*-1,3-diphenylpropene, as shown by comparison of its retention time and its infrared and ultraviolet spectra with those of an authentic sample. Its catalytic reduction (30% Pd–C, ethanol) yielded a sample whose infrared and ultraviolet spectra and vapor phase chromatographic retention time corresponded to those of authentic 1,3-diphenylpropane.

From a similar acetolysis, 1.7 g of hydrocarbon fraction was obtained from 10 g of tosylate. Vapor phase chromatography again showed two components, 15% of the above *cis*-1,3-diphenylpropene and 85% of a component with longer retention time. The latter was isolated and repeatedly recrystallized from hexane (Dry Ice–methanol), yielding a sample of *trans*-1,3-diphenylpropene, mp 15–17°, which was chromatographically homogeneous and displayed an infrared spectrum identical with that of an authentic sample. Its catalytic hydrogenation, as before, resulted in the uptake of 1 molar equiv of hydrogen and the formation of a product whose infrared and ultraviolet spectra and gas chromatographic retention time corresponded again to those of 1,3-diphenylpropane. Its bromination in chloroform afforded the crystalline 1,2-dibromo-1,3-diphenylpropane, mp 107–109.5°, reported by Dieckmann and Kämmerer.[35] The product had an infrared spectrum identical with and showed no mixture melting point depression with an authentic sample of this dibromide.

(35) W. Dieckmann and M. Kämmerer, *Ber.*, **39**, 3046 (1906).

The infrared spectra of the above 1.2 g of viscous syrup from the original benzene eluate showed strong bands at 1730 and 1245 cm^{-1}, suggesting a mixture of acetates. Vapor phase chromatography of the product (the above analytical column, 200°) showed seven peaks with retention times (in minutes) (relative intensity) as follows: (a) 2 (3.7), (b) 3.5 (3.1), (c) 4.3 (4.7), (d) 6.5 (6.0), (e) 7.8 (13.4), (f) 9.5 (2.8), and (g) 12.0 (0.5). Under the same conditions a crude sample of 2-tropyl-2-phenylethyl acetate showed a retention time of 7.8 min. The identities of these presumably ester products are currently under investigation.

Acetolysis of 2,3-Diphenyl-1-propyl *p*-Toluenesulfonate.—A solution containing the above tosylate (1.0 g), anhydrous sodium acetate (0.5 g), and a trace of hydroquinone in acetic acid (20 ml) was heated under reflux for 16 hr, then was cooled and poured into ice and water (175 g) containing sodium hydroxide (16 g). The mixture was extracted with ether, and the extract was washed with water, treated with methanol (5 ml), and evaporated to dryness under vacuum. Vapor phase chromatographic examination of the crude residue showed three peaks in a ratio of 25:120:196, the retention times of the first two matching those of *cis*- and *trans*-1,3-diphenylpropene. The entire sample was placed on a 1.8 × 2.0 cm column of silica gel G, which was eluted with petroleum ether (50 ml) followed by benzene (75 ml). Evaporation of the petroleum ether eluate yielded 0.20 g of colorless oil whose ultraviolet and infrared spectra matched those of the crude 1,3-diphenylpropene fraction from the previous acetolysis. Rechromatographing on silica gel G gave 0.15 g of colorless oil whose vapor phase chromatography showed two peaks corresponding in retention time to *cis*- and *trans*-1,3-diphenylpropene. Evaporation of the above benzene eluate afforded 0.50 g of colorless liquid whose infrared spectrum was consistent with that of an acetate. Vapor phase chromatography showed two peaks in a ratio of 1:5.3. The crude material was reduced to an alcohol (0.37 g) using lithium aluminum hydride in ether. The infrared spectrum of the alcohol product was identical with that of a sample of 1,3-diphenyl-2-propanol prepared by the lithium aluminum hydride reduction of dibenzyl ketone.

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Organic Fluorine Compounds. I. Reinvestigation of the Action of Perchloryl Fluoride on Diethyl Malonate[1]

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The reaction of perchloryl fluoride on diethyl malonate in the presence of strong base has been reexamined. Whereas it was previously reported that only one product, diethyl difluoromalonate, resulted from this reaction in ethanol, the present study established the presence of five products: diethyl difluoromalonate (I), diethyl ethylmalonate (II), diethyl malonate (III), diethyl ethylfluoromalonate (IV), and diethyl fluoromalonate (V). In an aprotic solvent, toluene, the reaction yielded only I, III, and V. The alcohol was shown to participate in a competing reaction. That these reactions are general was established by comparable studies with diethyl ethylmalonate and diethyl fluoromalonate.

It was reported by Inman and co-workers[2–5] that compounds containing active methylene groups could be fluorinated by perchloryl fluoride in the presence of strong base. These authors[3] stated that on fluorination of the sodium salt of diethyl malonate in ethyl alcohol only the difluoromalonate was produced. Even if insufficient sodium was used, the difluoromalonate and unreacted starting material were obtained. A quantitative yield of diethyl difluoromalonate was produced when 2 equiv of sodium/mole of diethyl malonate was employed. No monofluoromalonic ester was recovered under any of the fluo-

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(2) C. E. Inman, E. A. Tyczkowski, R. E. Oesterling, and F. L. Scott, *Experientia*, **14**, 355 (1958).

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(5) C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, U. S. Patent 3,141,040 (1964).