methyl iodide. Gc analysis (A, 125°; B, 175°) showed the principal products to be norcarane (**7**) and methylene iodide in a ratio of *ca.* 1:3. The bromonorcaranes (**5** and **6**) were each present in trace amounts. No trace of the 7-methylnorcaranes was present (estimated <5% relative to norcarane). The actual yield of norcarane was *ca.* the same as that in the preceding experiment.

Control Reactions of Methylene Bromide.—A solution of anhydrous lithium iodide (1.34 g, 0.01 mole) and methylene bromide (3.5 g, 0.02 mole) in anhydrous ether (6 ml) was stirred for 3 hr at room temperature, then processed in the usual manner. Gc analysis (B, 175°) showed no trace of methylene iodide (<1% yield).

Anhydrous lithium iodide (1.34 g, 0.01 mole) was added to a solution of methyllithium in ether (6 ml of 1.67 *M* solution, 0.01 mole, prepared from methyl chloride), and the resulting slurry was slowly added to methylene bromide (3.5 g, 0.02 mole) at *ca.* 10–30°. The reaction mixture was stirred for 3 hr at room temperature, then processed as above. Gc analysis indicated a 40% yield (based on lithium iodide) of methylene iodide.

Reaction of Cyclohexene with Bromoform and Methyllithium Prepared from Methyl Chloride.—A solution of methyllithium in ether (24 ml of 1.67 *M* solution, 0.04 mole, prepared from methyl chloride) was added dropwise over a period of 45 min to a stirred solution of cyclohexene (9.9 g, 0.12 mole) and bromoform (20.3 g, 0.08 mole) at 5–15°. An additional 5 ml of ether was then added. The reaction mixture was stirred for an additional 2 hrs at room temperature, then worked up as described above. Gc analysis (A, 150°) indicated an *ca.* 8% yield (based on methyllithium) of products in the following relative proportions: 86% 7,7-dibromonorcarane (**10**) and 9% *cis*- (**5**) and 5% *trans*-7-bromonorcarane (**6**). In addition a large number of unidentified components of short retention time were obtained. However a separate control reaction of bromoform and methyllithium prepared from methyl chloride showed that all of these components resulted from reactions which did not involve cyclohexene. There was no evidence of any norcarane (**7**) or the methylnorcaranes (**3** and **4**) (limit of detectability *ca.* 5%). The three bromo derivatives were isolated by preparative gc (A, 175°; B, 160°). The first two components eluted were identified as the *cis*- (**5**) and *trans*-bromo- (**6**) isomers: mass spectrum, *m/e* 174 (M^+, one bromine atom per molecule). The nmr spectra were in agreement with data reported in the literature[33].

The third component eluted was the dibromo derivative (**10**): mass spectrum, *m/e* 252 (M^+, two bromine atoms per molecule); nmr spectrum, a broad multiplet at −2.4 to −1.1 ppm with major peaks at −1.83 and −1.33 having an area ratio of ~6:4. The infrared spectrum was identical with that reported.[38]

Reaction of Cyclohexene with Bromoform and Methyllithium Prepared from Methyl Iodide.—The preceding experiment was repeated using methyllithium prepared from methyl iodide. Gc analysis of the product after work-up indicated an 8% yield (based on methyllithium) of norcarane derivatives in the following proportions: 91% **10**, 7% **5**, and 2% **6**. In addition a large number of unidentified components of short retention time were also obtained. A control reaction of bromoform and methyllithium prepared from methyl iodide, in the absence of cyclohexene, also gave these unidentified products. Norcarane (**7**) and the methylnorcaranes (**3** and **4**) were not evident, but their presence in relative amounts up to *ca.* 10% could not be ruled out because of the interference of the unidentified compounds mentioned above.

Registry No.—**1**, 1121-42-2; **2**, 1121-43-3; **3**, 14154-00-8; **4**, 14123-39-8; **5**, 1121-40-0; **6**, 1121-41-1; **7**, 286-08-8; **8**, 14123-41-2; **9**, 14172-83-9; **10**, 2415-79-4; cyclohexene, 110-83-8; methylene chloride, 75-09-2; methyllithium, 917-54-4; 2,3-dimethyl-2-butene, 563-79-1; methylene bromide, 74-95-3; bromoform, 75-25-2; methylene iodide, 75-11-6.

Acknowledgment.—We wish to thank Dr. J. C. Little, and Professors G. L. Closs, R. M. Magid, M. Stiles, and H. M. Walborsky for many helpful comments.

(38) W. v. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

Group Migrations to Carbene Centers. Pyrolysis of the Sodium Salts of α-Arylisobutyrophenone Tosylhydrazones

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Tosylhydrazones **1** of several α-arylisobutyrophenones have been synthesized, converted to the corresponding dry sodium salts, and thermally decomposed to give a mixture of aryl migration products **2** and carbon–hydrogen insertion products **4**, but no products of methyl migration. Protic decomposition of **1** resulted in the formation of **2**. The syntheses of all possible reaction products are described. Migratory aptitudes for the aryl groups follow: *m*-chlorophenyl, 0.67; phenyl, 1.0; *p*-tolyl, 1.90. The data followed σ^+ with $\rho = -0.68$.

The facile migration of hydrogen and aryl groups to carbene sites generated in several systems has long been recognized,[2] but relatively little systematic information on the detailed nature of the transition state for migration as a function, both of electronic interactions by substituents on the migrating group and substituents directly attached to the divalent carbon atom, is available.

In a recent study by Sargeant and Shechter,[3] the thermal decompositions of several 2,2-diphenyl-2-arylacetaldehyde tosylhydrazones were carried out in the presence of excess sodium methoxide in diethyl carbitol at 90° to give a mixture of products from which the migratory aptitudes for the aryl groups were calculated. The data fitted a Hammett plot (σ^+) with $\rho = -0.28$

$$\mathrm{Ar(Ph)_2CCH}\overset{\mathrm{NNHTs}}{\parallel} \rightarrow \mathrm{Ph_2C{=}CHAr} + \mathrm{PhArC{=}CHPh}$$

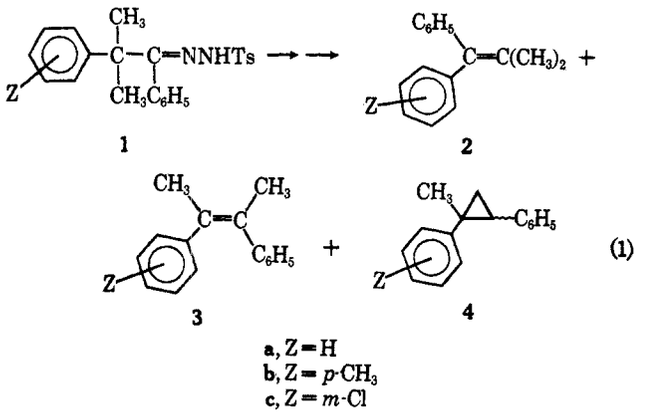
In the present study, the dry salts of several tosylhydrazones **1** have been prepared and thermally decomposed both in the absence of solvent and in ethylene glycol solution. The only expected products

(1) Taken from the Ph.D. Dissertation of A. G. K., University of Kansas, 1966. Partial support from National Science Foundation Grant Gp-3519 is hereby acknowledged.

(2) (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) J. Hine, "Divalent Carbon," Ronald Press, Inc., New York, N. Y., 1964.

(3) P. B. Sargeant and H. Shechter, *Tetrahedron Letters*, 3957 (1964).

which are of interest are those from aryl or methyl migration, **2** and **3**, and from carbon–hydrogen bond insertion, **4**, all but one of which were independently synthesized for Z = H, *p*-CH_3, and *m*-Cl (eq 1).



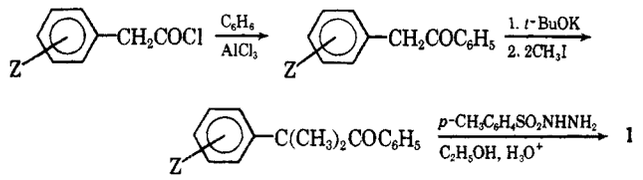
a, Z = H
b, Z = *p*-CH_3
c, Z = *m*-Cl

Since the relative amount of **4** produced would be predicted to be insensitive to the nature of substituent Z (see Discussion), migratory aptitudes were calculated directly from the ratio of migration product to carbon–hydrogen insertion product, by means of nmr analysis of the product mixture.

Because the carbene center generated from **1** under aprotic conditions is directly attached to an aromatic ring, future systematic studies of the electronic interactions of various functional groups with the divalent carbon atom are now feasible.

Synthesis.—The tosylhydrazones for this study were conveniently prepared according to the outline presented in Scheme I. Intermediates in the sequence

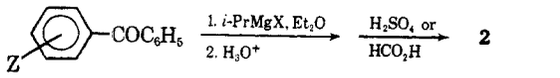
SCHEME I



were identified from their infrared and nmr spectra and by comparison of physical properties with those reported in the literature. The tosylhydrazones **1a–c**, prepared in low yield from the corresponding ketones, were contaminated with small amounts of the unchanged ketone. Numerous and varied attempts to obtain analytically pure **1a–c** under conditions which would not result in decomposition were unsuccessful. Nmr data provided unequivocal evidence for the structures (see Experimental Section).

The products which would result from an aryl migration to the carbene center were prepared from the appropriately substituted benzophenone by the addition of isopropylmagnesium halide followed by hydrolysis and treatment of the crude alcohol with 20–50% sulfuric acid or 85% formic acid at reflux (Scheme II). Compounds **2b** and **2c** which had not been previously reported were fully characterized by infrared, nmr,

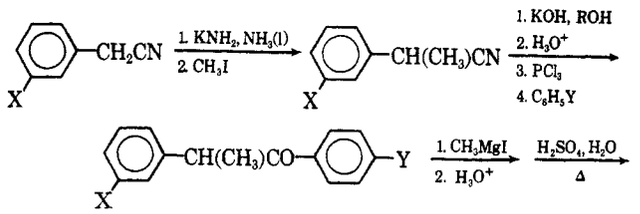
SCHEME II



and mass spectral data as well as by elemental analysis. The *gem*-dimethyl group of all three olefins appeared as a singlet at τ 8.20–8.23.

With the exception of α,α'-dimethylstilbene **3a** which was prepared from 1-phenylethyl chloride by the method of Kharasch and Kleiman,[4] the other olefinic products which would result from the migration of methyl to the carbene center were conveniently synthesized by the sequence of reactions outlined in Scheme III.

SCHEME III



3b (X = H, Y = CH_3) or **3c** (X = Cl, Y = H)

The previously unreported olefin **3b** gave the correct elemental analysis for $C_{17}H_{18}$. The infrared and nmr spectral data were consistent with the assigned structure. The sample was a mixture of the two geometrical isomers in a 57.5:42.5 ratio as indicated by vpc data and the fact that ozonolysis resulted only in an equimolar mixture of acetophenone and *p*-methylacetophenone.

The addition of methylmagnesium iodide to α-(*m*-chlorophenyl)propiophenone followed by dehydration of the product alcohol with 20% sulfuric acid or 85% formic acid at reflux resulted in the formation of 2-phenyl-3-(3-chlorophenyl)-1-butene instead of the desired product. Isomerization of the unwanted terminal olefin to **3c** was accomplished by use of concentrated sulfuric acid at 25° for 30 min followed by hydrolysis with crushed ice. Olefin **3c** was characterized by infrared and nmr spectral data and elemental analysis. Analytical vpc data indicated the presence of both geometrical isomers.

The nmr data for **3b** and **3c** deserve further comment. The chemical shifts of the methyl protons of olefins **3a** and **2b**, together with the knowledge that

TABLE I
CHEMICAL SHIFTS[a] OF METHYL SUBSTITUENTS FOR THE VARIOUS PRODUCTS OF DECOMPOSITION OF TOSYLHYDRAZONES **1**

Product	Olefinic methyls	Aromatic methyl
Styrene **2a**	8.23	
Styrene **2b**	8.20	7.70
Styrene **2c**	8.22	
Stilbene **3a**[b]	8.13; 7.87	
Stilbene **3b**[b]	8.13; 7.88	7.66, 7.82
Stilbene **3c**[b]	8.13, 8.20, 7.84	
Cyclopropane **4a**[b]	8.90, 8.50	
Cyclopropane **4b**[b]	8.94, 8.50	7.68, 7.78

[a] τ values taken in carbon tetrachloride. [b] Mixture of two isomers.

3b was a 60:40 mixture of geometrical isomers allowed an assignment of the four upfield singlets at τ 7.66, 7.82, 7.88, and 8.13 to be made (Table I) in that the 7.66 and 8.13 singlets are associated with the 40%

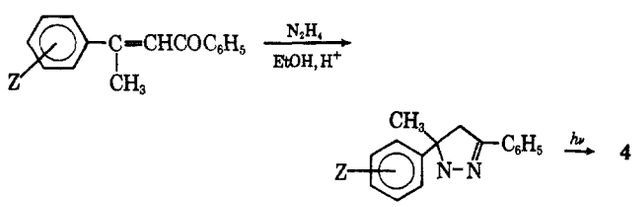
(4) M. S. Kharasch and M. Kleiman, *J. Am. Chem. Soc.*, **65**, 11 (1943).

isomer while the 7.82 and 7.88 singlets are associated with the 60% isomer. The upfield region of **3c** consists of three singlets at τ 7.84, 8.13, and 8.20. The nmr spectrum of the largest component of the geometrical isomer mixture collected by preparative vpc showed upfield singlets at 8.13 and 8.20 and represents the only isomer of structure **3** which shows nonequivalence of the methyl groups on the double bond.

Because the ultraviolet extinction coefficients of the isomers of stilbene **3a** strongly suggest that the isomer of higher boiling point (olefinic methyl at τ 8.13) is *trans*,[5] the *trans* stereochemistry can be tentatively assigned to those stilbene isomers with olefinic methyl groups at τ 8.1–8.2. However, it should be pointed out that such assignments are opposite those which would be made on the basis of expected diamagnetic anisotropic deshielding effects such as those observed for *cis*- and *trans*-stilbene.[6]

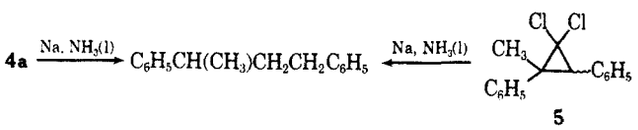
The preparation of the cyclopropane derivatives which would result from carbon–hydrogen bond insertion was carried out according to Scheme IV. The

SCHEME IV



pyrazolines, which were obtained as impure oils which decomposed slowly with the evolution of nitrogen, were irradiated with ultraviolet light (~2537 A) to give a mixture of the *cis* and *trans* isomers of desired cyclopropanes **4a** and **4b**.

Cyclopropane **4a** was characterized by infrared and nmr spectral data and a correct elemental analysis. Chemical verification of the structure of **4a** was obtained by reduction of the compound with sodium in liquid ammonia to give 1,3-diphenylbutane, the same



product that results from the reduction of dichlorocyclopropane **5**, prepared by the treatment of α-methylstilbene with phenyldichlorobromomethylmercury.

The geometrical isomer mixture of **4b** was separated by preparative vpc into two fractions which exhibited upfield cyclopropyl–methyl singlets at 8.50 and 8.90 respectively in addition to the aromatic methyl singlets at 7.78 and 7.68 (Table I). Although one of the isomers was contaminated by an olefinic impurity, nmr data provided unequivocal evidence for the structures and the pure isomer gave the correct analysis for $C_{17}H_{18}$.

Tosylhydrazone Salt Decomposition.—The thermal decomposition of *p*-toluenesulfonylhydrazones in the presence of a base or the decomposition of the corresponding salts has been shown to proceed *via* a carbene pathway only if precautions are taken to remove all proton sources,[7] including the tosylhydrazone itself.[8] The presence of protic material can result in the formation of the corresponding carbonium ion and a subsequent complication in the interpretation of the results.

In the present study, the dry sodium salts of tosylhydrazones **1a–c** were first prepared in tetrahydrofuran by the use of a fivefold excess of sodium methoxide.[9,10] The isolated salts were then kept at <0.1 mm of pressure for 30 min, followed by pyrolysis at 1 atm (N_2) at temperatures of 160–195°[11] until the evolution of nitrogen ceased.

The analysis of migration and insertion products was carried out by a direct nmr examination of the products isolated from an ether extract of the slurry of crude reaction mixture and water. Careful planimeter measurements were made of the upfield singlets corresponding to the various possible products (Table I).[12] The presence of less than 1% of a given product could readily be determined. The data are displayed in Table II. Duplicate runs resulted in an average deviation of less than ±2.3%.

TABLE II
PRODUCT DISTRIBUTION AND ARYL MIGRATORY APTITUDES FROM THE APROTIC DECOMPOSITION OF THE SODIUM SALT OF TOSYLHYDRAZONES 1[a,b]

Substituent Z of starting salt 1	% aryl migration product 2[c]	% C–H insertion product 4[c]	Aryl migratory aptitude[d]
H	72.8 ± 1.1	27.2 ± 1.1	1.00
p-CH_3	83.6 ± 2.3	16.4 ± 2.3	1.90
m-Cl	64.2 ± 1.0	35.8 ± 1.0	0.67

[a] Decomposition at 160–195°. [b] No methyl migration observed. [c] Error represents the average deviation of two runs. [d] Normalized ratio of aryl migration to C–H insertion.

Similar thermal decompositions of the same tosylhydrazone salts under protic conditions in ethylene glycol gave only products of aryl migration, **2a–c**.

Discussion

It should be noted that products **2**, **3**, and **4** represent 20–40% of the total product mixture. Similar thermal decompositions by Philip and Keating[13] have been shown to result in as much as 45–54% azine formation. No attempt was made to isolate and identify the azines formed by the decomposition of **1**.

The method for the determination of the relative migratory aptitudes listed in Table II is founded on the assumption that the relative amount of carbon–hydrogen insertion product **4** formed in each of the decompositions is essentially independent of the nature of substituent Z. In view of the decrease in an induc-

(5) H. Suzuki, *Bull. Chem. Soc. Japan*, **25**, 145 (1952).

(6) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958).

(7) (a) J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965), and references cited therein; (b) J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *ibid.*, **87**, 661 (1965).

(8) J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

(9) The use of sodium hydride has been shown to result in the formation of anomalous products attributed to the attack of hydride on the carbon–nitrogen double bond of the hydrazone.[10]

(10) R. M. McDonald and R. A. Krueger, *ibid*, **31**, 488 (1966).

(11) Migratory aptitudes determined by Sargeant and Shechter[3] were shown to be insensitive to changes in temperature.

(12) Although cyclopropane **4c** had not been prepared, it was assumed that the methyl chemical shifts for the two geometrical isomers would be similar to those of **4a** and **4b**, *i.e.*, τ 8.50 and 8.90. The nmr spectrum of the product mixture from the pyrolysis of the salt of **1c** exhibited singlets at 8.40 and 8.85 which were attributed to the expected cyclopropane **4c**.

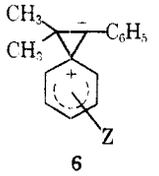
(13) H. Philip and J. Keating, *Tetrahedron Letters*, 523 (1961).

tive substituent effect by a factor of *ca.* 1:2.8 per methylene group,[14] the insulation of the carbon–hydrogen bond from the substituted aromatic ring by two methylene groups argues against any significant change in the relative amount of product **4** with a change in Z unless the transition state for insertion is quite polar. The fact that alkylcarbenes generated from tosylhydrazones insert with little discrimination into primary and secondary carbon–hydrogen bonds unless there are specific steric interactions present[15] suggests that the transition state is relatively nonpolar. Similarly, since even a drastic change in the substituent directly attached to a divalent carbon atom has only a small effect on the relative rate of insertion into tertiary *vs.* primary carbon–hydrogen bonds,[16,17] it seems unlikely that changing the substituent on an aromatic ring insulated from the divalent carbon atom by a methylene group would cause a significant change in the ground-state energy of the carbene and therefore in the carbon–hydrogen insertion rate.

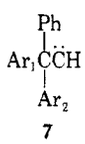
Although the aryl migratory aptitudes listed in Table II clearly indicate a stabilization of the transition state by electron donar substituents on the migrating group, the magnitude of the effect is somewhat smaller than that for the rearrangement of aryl groups in carbonium ion reactions. For example, Bachmann and Ferguson[18] have reported that in the pinacol–pinacolone rearrangement of symmetrically substituted aromatic pinacols in the presence of acetic acid and benzene (100°) the relative migratory aptitudes for *m*-chlorophenyl and *p*-tolyl were 0 and 500, respectively.

It is particularly significant that an extrathermodynamic relationship for the data of Table II with σ^+ exists and exhibits $\rho = -0.68$, a value somewhat larger than the -0.28 reported by Sargeant and Shechter[3] for the thermal decompositions of 2,2-diphenyl-2-arylacetaldehyde tosylhydrazones, *vide supra*. Unfortunately a critical comparison of the values cannot be made since the two studies were carried out at considerably different temperatures and no data on the temperature dependence of ρ are available. The present results for **1** imply that substantial charge separation exists in the transition state for the migration as represented in structure **6**.[19]

It should be noted that in the work of Sargeant and Shechter,[3] the nature of Ar_2 (structure **7**) had a small influence on the migratory aptitude of Ar_1,[20] a fact which prompted them to report some transition-state charge delocalization to the migration origin. The effect of the presence of two methyl groups at the migration origin in the carbene generated from **1** cannot be assessed from the available data, but one would assume that charge delocalization of the type described above for **7** would be less important in the present case.

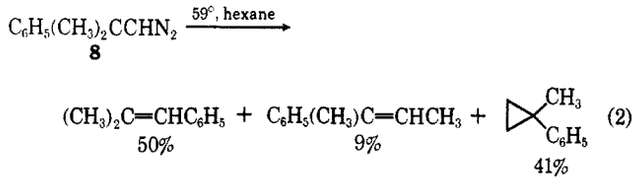


6



7

Except for carbenes generated in or adjacent to strained small-ring systems[7,21] or systems with specific conformational requirements,[22] alkyl migrations are generally not observed, or occur to a very limited extent.[2,3] Less than 1% methyl migration was observed for the aprotic decomposition of the sodium salt of **1**. This is in contrast to the report by Philip and Keating[13] that the thermal decomposition of diazo compound **8** (eq 2) produced a 10:1 ratio of



$$\underset{\mathbf{8}}{C_6H_5(CH_3)_2CCHN_2} \xrightarrow{59^\circ,\ \text{hexane}} \underset{50\%}{(CH_3)_2C{=}CHC_6H_5} + \underset{9\%}{C_6H_5(CH_3)C{=}CHCH_3} + \underset{41\%}{\text{(CH}_3\text{, C}_6\text{H}_5\text{)}} \quad (2)$$

phenyl to methyl migration or a relative yield of 9% of the methyl migration product.

As expected, the decomposition of **1** in the presence of sodium methoxide and ethylene glycol resulted in no detectable methyl migration or carbon–hydrogen insertion.

Experimental Section[23]

α-Phenylisobutyrophenone.—The compound was prepared by a procedure patterned after that of Johnson and Daub,[24] in which a solution of potassium *t*-butoxide prepared from potassium (21.1 g, 0.54 g-atom) and dry (calcium hydride) *t*-butyl alcohol (400.2 g, 5.4 moles) was maintained at reflux for 5 hr after the addition of deoxybenzoin (35.5 g, 0.18 mole) after which methyl iodide was slowly added (45 min) and the reaction mixture was heated for an additional 12-hr period. After the usual work-up, distillation afforded a liquid product which showed an nmr spectrum consisting of a multiplet at 2.05 (2 H), a multiplet at 2.74 (8 H), and a singlet at 8.47 (6 H). The infrared spectrum showed significant absorptions at 1680 (benzoyl), 1280, and 1365 cm^{-1} (*gem*-dimethyl). The 2,4-dinitrophenylhydrazone was prepared.

Anal. Calcd for $C_{22}H_{20}N_4O_4$: C, 65.34; H, 4.98; N, 13.85. Found: C, 65.33; H, 5.09; N, 14.33.

α-Phenylisobutyrophenone Tosylhydrazone (1a).—The compound was prepared by the method of Bamford and Stevens[25] as a gum which was redissolved in ethanol, dried twice with anhydrous magnesium sulfate, and isolated as a white precipitate by evaporation. Recrystallization from chloroform gave material which showed one component by tlc, mp 131–135° dec.

(14) R. W. Taft, Jr. in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 592.

(15) (a) G. L. Closs, *J. Am. Chem. Soc.*, **84**, 809 (1962); (b) W. Kirmse and G. Waechtershaeuser, *Tetrahedron*, **22**, 63 (1966).

(16) The tertiary to primary carbon–hydrogen insertion rate ratios for methylene and carbomethoxy carbene differ by a factor of only 2.4.[17]

(17) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

(18) W. E. Bachmann and J. W. Ferguson, *ibid.*, **56**, 2081 (1934).

(19) The possibility that aryl migration is concerted with loss of nitrogen from the intermediate diazo compound cannot be rigorously excluded.

(20) A change in Ar_2 from phenyl to *p*-tolyl caused a decrease in the migratory aptitude of *p*-tolyl by 19%.

(21) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960); (b) W. Kirmse and K. H. Pook, *Chem. Ber.*, **98**, 4022 (1965); (c) F. T. Bond and D. E. Bradwag, *J. Am. Chem. Soc.*, **87**, 4977 (1965).

(22) (a) J. W. Wilt, J. M. Kosturik, and R. C. Orlowski, *J. Org. Chem.*, **30**, 1052 (1965); (b) J. W. Wilt, J. F. Zawadzki, and D. G. Schultenover, *ibid.*, **31**, 876 (1966).

(23) All nmr spectra were measured in carbon tetrachloride with a Varian A-60 spectrometer; chemical shift values are expressed on the τ scale. All infrared spectra, unless otherwise specified, were obtained in carbon tetrachloride with a Perkin-Elmer Infracord or a Beckman Model IR-8 double-beam recording spectrometer with sodium chloride optics; a 1601-cm^{-1} polystyrene absorption was used as a standard. Vapor phase chromatography (vpc) was done on either an Aerograph Hi-Fi Model 600 equipped with a hydrogen flame detector, an F & M Model 700 equipped with a hydrogen flame detector and a thermal conductivity detector, or an Aerograph Autoprep Model A-700 equipped with a thermal conductivity detector. All the chromatographs were equipped with a Disc integrator. Chemical analyses were performed by either Huffman Laboratories, Inc., Wheatridge, Col., or by Galbraith Laboratories, Inc., Knoxville, Tenn.

(24) W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 72 (1952).

(25) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

The nmr spectrum showed, in addition to complex multiplets in the aromatic region, singlets at 8.38 and 8.61 (*gem*-dimethyl of the two geometric isomers), a singlet at 7.52 (*p*-CH_3), a barely detectable broad absorption at ~6.2 (NH), and a singlet at 8.47 (*gem*-dimethyl of the contaminant starting ketone). The infrared spectrum showed characteristic absorptions at 1380 and 1162 cm^{-1} for the sulfonamide group and no carbonyl absorption.

4-Methyldeoxybenzoin.—Crude 4-methylphenylacetic acid prepared in 89% yield by carbonation of the Grignard reagent of 4-methylbenzyl chloride, was converted to 4-methyldeoxybenzoin by the method of Allen and Barker[26] in 51.5% yield, mp 90.5–93.0 (lit.[27] 97°). The nmr spectrum showed multiplets at 2.09, 2.57, and 2.96 (9 H), a singlet at 5.89 (2 H), and a singlet at 7.70 (3 H). The infrared spectrum showed the presence of a carbonyl group.

α-(*p*-Tolyl)isobutyrophenone was prepared by the same procedure used for the preparation of α-phenylisobutyrophenone. The crude yellow oil, bp 150–170° (2 mm), gave an infrared spectrum which showed significant absorptions at 1680, 1380, 1362, and 1500 cm^{-1}. The nmr spectrum showed multiplets at 2.14 and 2.83 (4 H), a singlet at 7.67 (3 H), and a singlet at 8.46 (6 H). The 2,4-dinitrophenylhydrazone was prepared.

Anal. Calcd for $C_{23}H_{22}N_4O_4$: C, 66.03; H, 5.30; N, 13.39. Found: C, 65.87; H, 5.07; N, 13.30.

α-(*p*-Tolyl)isobutyrophenone Tosylhydrazone (1b).—α-(*p*-Tolyl)isobutyrophenone (11.0 g, 0.027 mole) was added to a stirred solution of *p*-toluenesulfonylhydrazine (5.0 g, 0.027 mole) in 1 *N* hydrochloric acid in 95% ethanol, heated for 30 min on a steam bath and stirred overnight. Evaporation of the solvent gave an oil which slowly crystallized from methylene chloride, mp 110–170° dec. *p*-Toluenesulfonylhydrazine (mp 107–108°) was present as an impurity. The infrared spectrum was nearly identical with that of the tosylhydrazone of α-phenylisobutyrophenone with the exception that a medium intensity peak was present at 1675 cm^{-1} and assigned to starting ketone. The nmr spectrum showed a multiplet at 2.75 and singlets at 7.45, 7.70, 8.42, and 8.6 in agreement with the assigned structure. Smaller impurity absorptions could be seen at 2.2, 3.2, and 7.6. The NH absorption was not clearly visible because of the low signal to noise ratio for the sample.

3-Chlorodeoxybenzoin.—(3-Chlorophenyl)acetic acid (24.1 g, 0.141 mole) prepared in 99% yield by carbonation of the Grignard reagent of 3-chlorobenzyl chloride, mp 69–71° (lit.[28] mp 74°) was treated with phosphorous trichloride (13.7 g, 0.100 mole) and the resulting acid chloride was used to acylate benzene (400 ml) in the presence of aluminum chloride (26.7 g, 0.20 mole). The product (14.9 g, 0.065 mole), mp 38–40° (lit.[29] mp 43°) was formed in an over-all yield of 45.7% of the theoretical amount.

α-(*m*-Chlorophenyl)isobutyrophenone was prepared in the same manner as α-phenylisobutyrophenone. The product (5.3 g, 0.0205 mole, 40%) was a colorless liquid, bp 130–134° (0.065 mm). The nmr spectrum showed multiplets at 2.08 and 2.71 (9 H) and a singlet at 8.45 (6 H).

α-(*m*-Chlorophenyl)isobutyrophenone tosylhydrazone (1c) was prepared from the ketone (5.3 g, 0.0205 mole) and *p*-toluenesulfonylhydrazine (5.0 g, 0.027 mole) dissolved in 65 ml of 1 *N* hydrochloric acid and several milliliters of 95% ethanol. After 6 weeks the solution gave an oil which was retreated with more *p*-toluenesulfonylhydrazine (5.0 g, 0.027 mole) in a solution of 100 ml of 1-butanol and 50 ml of 1 *N* hydrochloric acid. After an 11-hr reflux period and ether extraction, an oil was obtained which gave an infrared spectrum that showed absorptions characteristic of sulfonamide as well as a small amount of conjugated carbonyl group impurity. The nmr spectrum consisted of a multiplet at 2.72 and singlets at 7.59, 8.40, and 8.64 consistent with the structural assignment.

1,1-Diphenyl-2-methylpropene (2a) was prepared by allowing 1,1-diphenyl-2-methyl-1-propanol to reflux with 20% sulfuric acid for 1.5 hr followed by separation of the organic layer and distillation, bp 142–150 (0.8–1.6 mm). The crude light yellow oil was purified by preparative vpc on a 10 ft × 0.25 in. o.d. column of 6% SE-30, 4% E-600 on 30–60 mesh Chromosorb P to give a colorless liquid, $n^{24}D$ 1.5861 (lit.[30] $n^{23.5}D$ 1.586). The nmr spectrum showed a multiplet at 2.88 (10 H) and a singlet at 8.23 (6 H).

α,α′-Dimethylstilbene (3a) was prepared by the method of Kharasch and Kleiman[4] in 40% over-all yield as the impure *trans* isomer, recrystallized from methanol, mp 90–100° (lit.[4,5,31] *cis* mp 66–67°, *trans* 105°). The infrared spectrum showed an absorption at 1600 cm^{-1} and the absence of a carbonyl group. The nmr spectrum showed a multiplet at 2.78 (10 H) and a singlet at 8.13 (6 H).

Treatment of the product with pumice impregnated with concentrated sulfuric acid for 18 hr in cyclohexane at reflux resulted in a mixture of *cis* and *trans* **3a** in addition to some **2a**. The nmr spectrum showed upfield singlets at 7.87, 8.13, and 8.23.

α-Methylstilbene.—Methylmagnesium iodide, prepared from methyl iodide (21.3 g, 0.15 mole) and magnesium turnings (3.6 g, 0.15 g-atom) in diethyl ether (100 ml) was maintained at reflux for 3.5 hr after deoxybenzoin (19.3 g, 0.098 mole) had been added. After the usual work-up, the oily residue was kept at reflux with 20% sulfuric acid for 2.5 hr. The cooled solution was extracted with ether and chloroform, and the organic extracts were dried over magnesium sulfate and evaporated to an off-white solid which was recrystallized from 90% ethanol to give white crystals (15.6 g, 0.0804 mole, 84%) mp 79–81° (lit.[32] mp 82°). The nmr spectrum showed a multiplet at 2.70 (10 H), a singlet at 3.16 (1 H), and two singlets at 7.70 and 7.76 (3 H).

1,1-Dichloro-2,3-diphenyl-2-methylcyclopropane (5).—A mixture of α-methylstilbene (3.5 g, 0.018 mole), phenyl(bromodichloromethyl)mercury[33] (9.4 g, 0.021 mole), and benzene (45 ml) was heated and stirred at 85–90° in an argon atmosphere for 2.25 hr.[34] The phenylmercuric bromide was filtered from the cooled solution and a yellow oil was isolated from the solution in 100% yield (4.9 g, 0.018 mole). The infrared spectrum (CS_2) showed significant bands at 3100–2860, 1590, and 1460 cm^{-1}. The nmr spectrum showed a multiplet at 2.68 (10 H), a singlet at 6.89 (1 H), and a singlet at 8.60 (3 H).

Treatment of 1,1-Dichloro-2,3-diphenyl-2-methylcyclopropane with Sodium in Liquid Ammonia.—Sodium (2.0 g, 0.087 g-atom) was dissolved in liquid ammonia (75 ml) followed by the addition of the dichlorocyclopropane **5** (4.4 g, 0.0159 mole) in ether (25 ml) in accordance with the procedure of Closs and Closs.[35] After 1 hr, ammonium chloride (2.0 g) was added and the ammonia was allowed to evaporate. The residue, a yellow oil (1.5 g), gave a positive Beilstein test and was therefore further purified by treatment with lithium dispersion (2% sodium, 90% of particle size <15 μ) (20 g) in dry pentane at reflux for 16 hr followed by the addition of water and the usual extraction procedure. The product, bp 86–90° (0.06–0.1 mm), gave a single vpc peak on 20% Carbowax 20M, 6% SE-30 + 4% E-600, and 15% QF-1 all on 30–60 mesh Chromosorb P and a negative Beilstein test.

The infrared spectrum (CS_2) showed prominent absorptions at 3090–2860, 1590, and 1430 cm^{-1}. The nmr spectrum showed a multiplet (essentially two large peaks) at 2.88 (10 H), a multiplet at 7.10–7.70 (4 H), a multiplet at 7.90–8.40 (2 H), and a doublet at 8.74 (3 H, J = 6.5 cps). The mass spectrum gave a parent peak at m/e 210 and significant fragment ions at 15, 43, 58, 91, 105, 129, 131, and 132. The structure 1,3-diphenylbutane was assigned. An authentic sample of 1,2-diphenyl-2-methylcyclopropane when treated under the same conditions with sodium in liquid ammonia gave the same product, *vide infra*.

Dypnone was prepared in 44.5% yield by the method of Calloway and Green[36] from acetophenone (120 g, 1.0 mole) and aluminum chloride (66.7 g, 0.5 mole) in carbon disulfide

(26) C. F. H. Allen and W. E. Barker, *Org. Syn.*, **2**, 156 (1955).

(27) "Dictionary of Organic Compounds," Vol. 5, Oxford University Press, New York, N. Y., 1965, p 3080.

(28) "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, N. Y., 1965, p 674.

(29) See ref 28, p 675.

(30) W. J. Hickinbottom and G. E. M. Moussa, *J. Chem. Soc.*, 4195 (1957).

(31) M. Ramart-Lucas and E. Salmon-Logagneur, *Bull. Soc. Chim. France*, **45**, 718 (1929).

(32) "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, New York, N. Y., 1965, p 1293.

(33) (a) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965); (b) D. E. Lake and A. A. Asadorian (Dow Chemical Co.), U. S. Patent 2,553,518 (May 1951).

(34) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

(35) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

(36) N. O. Calloway and L. D. Green, *ibid.*, **59**, 809 (1937).

(500 ml). The product (49.3 g, 0.222 mole) was purified by a careful distillation, bp 160–166° (1 mm) (lit.[34] bp 160–165° (1 mm)).

3,5-Diphenyl-5-methyl-Δ^2-pyrazoline.—The technique of Kohler[37] was used. Dypnone (3.0 g, 0.0135 mole) was added to a solution of anhydrous hydrazine (3 g) in 95% ethanol (10 ml) which contained a few drops of glacial acetic acid. After the solution was stirred and maintained at reflux for 2 hr, the solvent was evaporated and the residue was distilled to give a viscous yellow oil, bp 170–176 (0.08 mm), which effervesced upon exposure to light and air, and when it came into contact (as a solution in CCl_4) with the salt plates of several infrared cells. The nmr spectrum showed multiplets at 2.40 and 2.72 (10 H), a broad singlet at 4.24 (1 H), a singlet at 6.98 (2 H), and a singlet at 8.53 (3 H).

1,2-Diphenyl-1-methylcyclopropane (4a) was prepared by the general procedure of Van Auken and Rinehart.[38] Freshly prepared 3,5-diphenyl-5-methyl-Δ^2-pyrazoline (10 g) was added to 2.5 times its volume of carbon tetrachloride in a Vycor test tube (2 × 16 cm) attached to an eudiometer tube. The mixture was irradiated (2537 A) in a "Rayonet" Photochemical Reactor at 40° until nitrogen evolution ceased (78.5 hr). The dark brown solution was filtered and concentrated to a viscous oil which was distilled on a 4-cm Vigreux column to give two fractions, bp 83–90° and 90° (0.05 mm). Vpc (20% Carbowax 20M on 45–60 mesh Chromosorb P, 10 ft) show one and two components, respectively, for the fractions.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: (83–90° fraction) C, 92.41; H, 7.71; (90° fraction) C, 90.87; H, 7.57.

The infrared spectrum showed significant absorptions at 3100–2880, 1600, 1500, 1460, 1440, and 1028 cm^{-1}. The nmr spectrum showed an aromatic multiplet at 2.70–3.45 (10 H), a cyclopropyl methine hydrogen multiplet at 7.50–8.00 (1 H), and a methylene multiplet at 8.50–8.90 together with two singlets at 8.50 and 8.90 respectively assigned to the methyl groups of the two geometric isomers (5 H total). The molecular weight (ebullioscopic method, chloroform) was 206 (calcd for $C_{16}H_{16}$: 208).

Reduction of 1,2-Diphenyl-1-methylcyclopropane (3c) with Sodium in Liquid Ammonia.—1,2-Diphenyl-1-methylcyclopropane (0.2 g, 0.000962 mole) in dry ether (5 ml) was slowly added to a stirred solution of sodium (0.5 g, 0.0218 g-atom) in liquid ammonia (60 ml). After 1 hr, ammonium chloride (2 g) was added and the ammonia was allowed to evaporate. The residue was washed with ether and the ether extracts were concentrated to a yellow oil which was distilled, bp 90–92° (0.08 mm). The nmr spectrum was superimposible with that of 1,3-diphenylbutane identified as the reduction product from cyclopropane **5**, *vide supra*.

1-Phenyl-1-*p*-tolyl-2-methylpropene (2b).—4-Methylbenzophenone (49.0 g, 0.25 mole, Aldrich) in 100 ml of ether was added to isopropylmagnesium chloride prepared from isopropyl chloride (31.4 g, 0.40 mole, distilled from calcium hydride) and magnesium turnings (9.71 g, 0.40 g-atom) in ether (300 ml). After a 9.5-hr reflux period, the reaction was worked up in the usual manner to give an oil which was kept at reflux with 50% sulfuric acid (300 ml) for 6 hr. The liquid product from an ether extract was distilled, bp 98–100° (0.08–0.07 mm). The product was purified by preparative vpc (10% QF-1 on 30–60 mesh Chromosorb P, 10 ft × 0.25 in.).

The infrared spectrum showed prominent absorptions at 1600, 1380, and 1370 cm^{-1}. The nmr spectrum showed singlets at 2.86 and 3.00 (9 H), at 7.70 (3 H), and at 8.20 (6 H). The mass spectrum gave a parent peak at *m/e* 222 and fragments at 15, 26, 43, 58, 91, 105, 115, 129, 188, 190, 191, 207.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.96; H, 8.16.

α-Phenylpropionitrile.—The combined procedures of Baldinger and Nieuwland,[39] and McElvain and Stevens[40] were used. Phenylacetonitrile (125 g, 1.065 moles) was slowly added to a solution of sodium (24.5 g, 1.065 g-atoms) in liquid ammonia (500 ml) which contained a small amount of dry ferric chloride. Methyl iodide (151 g, 1.065 moles) was added the mixture was allowed to stand 30 min, the ammonia was evaporated with a water bath, and the residue after being treated with dilute acid and extracted into ether was dried with calcium chloride and concentrated. The crude product was treated with benzaldehyde (36 g) and sodium methoxide (5 g) at room temperature (2 hr) to convert phenylacetonitrile to the condensation product. After the mixture had been heated on a steam bath 15 min, an equal volume of benzene was added and the solution was washed with water and a saturated aqueous solution of sodium bisulfite. The solid was filtered and the benzene was evaporated to give the product nitrile (61.3 g, 0.467 mole, 44%), bp 92–94° (5–6 mm) (lit.[40] bp 92–94° (6 mm)), $n^{25}D$ 1.5126 (lit.[38] $n^{25}D$ 1.5115).

The nmr spectrum showed a singlet at 2.73 (5 H), a quartet at 6.22 (1 H, J = 7.5 cps), and a doublet at 8.45 (3 H, J = 7.5 cps).

α-Phenylpropionic Acid.—The procedure was patterned after that of Prout and co-workers.[41] α-Phenylpropionitrile (29.3 g, 0.223 mole), potassium hydroxide (46 g, 0.8 mole), and ethylene glycol were maintained at reflux for 14 hr, cooled, diluted with water, and extracted with ether. The acidified aqueous layer was extracted with benzene which was dried, concentrated, and distilled to give the acid product (27.4 g, 0.182 mole, 81.5%), bp 134–136° (7 mm) (lit.[42] bp 161 (24 mm)).

The infrared spectrum showed significant absorptions at 3300–2500 and 1700 cm^{-1}. The nmr spectrum showed a singlet at −1.73 (1 H), a multiplet at 2.83 (5 H), a quartet at 6.36 (1 H, J = 7 cps), and a doublet at 8.55 (3H, J = 7 cps).

α-Phenyl-*p*-methylpropiophenone.—The general procedure of Bruzau[43] was used. 2-phenylpropanoic acid (30 g, 0.2 mole) was treated with phosphorus trichloride (11 g, 0.08 mole) at 60–65° for 1 hr according to the method of Kenyon and Young.[44] The upper layer of the cooled (ice bath) solution was added to a slurry of aluminum chloride (40 g, 0.3 mole) in toluene (100 ml) and the dark solution was heated until hydrogen chloride evolution ceased (1 hr), was cooled, and then poured onto crushed ice. The ether extract was washed with sodium bicarbonate solution, dried over magnesium sulfate, and concentrated to give crude product which was distilled, bp 174–180° (8 mm), and redistilled to give a pale yellow viscous liquid (17.3 g, 0.0771 mole, 38.6%) (lit.[43] mp 46–47°).

The infrared spectrum showed a carbonyl group at 1680 cm^{-1} and the absence of a carboxyl group. The nmr spectrum showed a doublet at 2.21 and a multiplet at 2.85 (9 H), a quartet at 5.45 (1 H, J = 7 cps), a singlet at 7.78 (3 H), and a doublet at 8.54 (3 H, J = 7 cps).

2-*p*-Tolyl-3-phenyl-2-butene (3b).—α-Phenyl-*p*-methylpropiophenone (17.2 g, 0.0766 mole) was slowly added to a diethyl ether solution of methylmagnesium iodide prepared from methyl iodide (16.3 g, 0.115 mole) and magnesium (2.8 g, 0.115 g-atom) and the solution was stirred for 12 hr at 25°, maintained at reflux for 30 min, hydrolyzed with dilute hydrochloric acid, and extracted with ether. The crude product was kept at reflux for 2 hr with 50% sulfuric acid. The aqueous layer was extracted with ether and worked up in the usual manner to give a liquid product, bp 103–113° (0.13 mm). Further distillation on a Teflon annular still at 141° with a 20:1 reflux ratio removed most of the ketone impurity. Preparative vpc (10% QF-1, 0.25 in. × 10 ft) gave the pure olefin.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.88; H, 8.11.

The infrared spectrum showed significant absorption at 3100–2860, 1600, 1500, 1480, 1440, and 1371 cm^{-1}. The nmr spectrum showed singlets at 2.80, 2.92, 3.07, and 3.22 (9 H), and additional singlets at 7.66, 7.82, 7.88, and 8.13 (9 H).

Ozonolysis of 2-*p*-Tolyl-3-phenyl-2-butene (3b).—The olefin (1.01 g) in glacial acetic acid (20 ml) was treated with ozone Welsbach Ozonator, 6 g of O_3 per hour as a 2% weight concentration in pure oxygen) for 30 min at 0°. The solution was poured into 150 ml of distilled water, stirred for 10 min, extracted with ether, and concentrated to a pale yellow liquid. Distillation at 1 atm gave a clear fraction which showed two peaks on vpc (5% SE-30 on Chromosorb P) at 5.2 min (acetophenone) and 8.1–8.4 min (*p*-methylacetophenone) in relative amounts of 55 and 45%, respectively. Retention times were compared with those of authentic samples under identical conditions.

(37) E. P. Kohler, *J. Am. Chem. Soc.*, **42**, 375 (1909).
(38) T. V. Van Auken and K. L. Rinehart, Jr., *ibid.*, **84**, 3736 (1962).
(39) L. H. Baldinger and J. A. Nieuwland, *ibid.*, **55**, 2851 (1933).
(40) S. M. McElvain and C. L. Stevens, *ibid.*, **69**, 2663 (1947).
(41) F. S. Prout, R. J. Hartman, E. P. -Y. Huang, C. J. Korpics, and G. R. Tichelaar, *Org. Syn.*, **4**, 95 (1963).
(42) H. S. Raper, *J. Chem. Soc.*, **123**, 2557 (1923).
(43) Mme. Bruzau, *Compt. Rend.*, **196**, 122 (1933).
(44) J. Kenyon and D. P. Young, *J. Chem. Soc.*, 263 (1941).

p-Methyl-β-methylcinnamic Acid.—A procedure analogous to that of Rupe and Wiederkehr[45] was used. Zinc dust was washed with dilute aqueous sodium hydroxide solution, distilled water, dilute aqueous acetic acid, distilled water, 95% ethanol, acetone, and ether, respectively. The dust was collected on a Büchner funnel and sucked dry under a rubber dam until the temperature reached 25°.

Zinc (32.7 g, 0.5 g-atom) and dry benzene (50 ml) were maintained at reflux while a solution of ethyl bromoacetate (67 g, 0.40 mole) and *p*-methylacetophenone (33.5 g, 0.25 mole) in dry benzene (90 ml) was slowly added. After an additional 6-hr reflux period, the cooled reaction mixture was stirred with cold (0°) 20% sulfuric acid and the solution was extracted with ether which was evaporated. The nmr spectrum indicated the presence of considerable starting alcohol. Dehydration was effected by treating the crude sample with formic acid, 85%, at reflux for 2 hr followed by the usual work-up procedure. The final olefin product was distilled, bp 112–116° (2 mm).

The infrared spectrum showed significant absorptions at 3100–2875, 1710, 1625, 1600 (sh), 1510, 1440, 1380, 1370, and 1340 cm^{-1}. The nmr spectrum showed a multiplet at 2.78 (*ca.* 4 H), a multiplet at 3.92 (1 H), a quartet at 5.85 (2 H, $J = 7$ cps), a singlet at 7.47 (3 H), a singlet at 7.68 (3 H), and a triplet at 8.74 (4 H, $J = 7$ cps).

The ester was hydrolyzed with 10% sodium hydroxide (200 ml) at reflux for 24 hr. The solid acid (18.1 g, 0.103 mole, 41% based on the ketone) had mp 131–133° (lit.[45] mp 135°).

1-Benzoyl-2-(*p*-tolyl)propene.—Phenyllithium from bromobenzene (53.4 g, 0.34 mole) and lithium wire (4.62 g, 0.68 g-atom) in 250 ml of dry ether was prepared according to the method of Jones and Gilman.[46] *p*-Methyl-β-methylcinnamic acid (6.0 g, 0.034 mole) was slowly added as an ether solution (250 ml). The reaction mixture was maintained at reflux for 10 hr, cooled, and hydrolyzed with water. An ether extract of the aqueous solution was dried, evaporated, and distilled to give the product (5.7 g, 0.0241 mole, 35.5%).

The infrared spectrum showed significant absorption at 3100–2880, 1660, 1600, 1510, 1445, 1430, 1375, and 1350 cm^{-1}. The nmr spectrum showed multiplets at 2.08, 2.63, and 2.85 (10 H), two peaks centered at 7.48 (3 H, with a separation of 1.5 cps), and a singlet at 7.70 (3 H) superimposed on a smaller impurity multiplet.

3-Phenyl-5-methyl-5-*p*-tolyl-Δ²-pyrazoline.—The same procedure was used as for the preparation of 3,5-diphenyl-5-methyl-Δ²-pyrazoline. The crude oily product from 2 g (0.00845 mole) of the ketone gave an nmr spectrum which showed multiplets at 2.47 and 2.80 (*ca.* 9 H), a singlet at 4.86 (1 H), a singlet at 6.97 (2 H), a singlet at 7.72 (3 H), and a singlet at 8.48 (3 H). The infrared spectrum could not be obtained because the material effervesced when placed into contact with the sodium chloride windows.

Photolysis of 3-Phenyl-5-methyl-5-*p*-tolyl-Δ²-pyrazoline.—The crude pyrazoline was dissolved in four times its volume of carbon tetrachloride in a Vycor test tube and irradiated (2537 A) at 40° in a "Rayonet" Photochemical Reactor until nitrogen evolution ceased (54 hr). The dark brown solution was filtered and concentrated to a viscous oil which was distilled, bp 125–144° (0.65–0.06 mm). The crude product was separated into two fractions by preparative vpc (20% QF-1 on 30–60 mesh Chromosorb P, $^3/_8$ in. × 10 ft). The first fraction was shown by analytical vpc to be a mixture of two compounds (60:40), bp 90–100° (0.07 mm), while the second fraction appeared to be one compound, bp 98–100° (0.05 mm).

The infrared spectrum of fraction 1 showed absorptions at 3100–2880, 1600, 1510, 1490, 1440, 1110, 1085, 1060, 1030, 1020, and 895 cm^{-1}. The nmr spectrum showed a multiplet from 2.72–3.40, a singlet at 4.62, singlets at 7.64 and 7.78, a small singlet at 8.00, and a singlet at 8.50 superimposed on a multiplet from 8.50–9.00. The approximate area ratios were 9:0.8:1.6:0.5:3.0.

The infrared spectrum of fraction 2 showed absorptions at 3100–2880, 1600, 1510, 1495, 1445, 1110, 1075, and 1020 cm^{-1}. The nmr spectrum showed a multiplet at 2.77 (9 H), a singlet at 7.68 superimposed on a multiplet at 7.50–7.80 (4 H), and a singlet at 8.94 superimposed on a multiplet at 8.50–9.00 (5 H). The elemental analysis is given below. Structure assignments are prescribed in the Discussion.

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.75; H, 8.31.

(45) H. Rupe and Fr. Wiederkehr, *Helv. Chim. Acta.*, **7**, 654 (1924).

(46) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 353 (1951).

1-Phenyl-1-(3-chlorophenyl)-2-methylpropene (2c).—3-Chlorobenzophenone (21.7 g, 0.1 mole), mp 82–83° (lit.[47] mp 82–83°), in diethyl ether (150 ml) was slowly added to a solution of isopropylmagnesium bromide prepared from isopropyl bromide (61.5 g, 0.5 mole) and magnesium turnings (12.16 g, 0.5 g-atom) in dry diethyl ether. After being maintained at reflux for 3 hr, the solution was cooled, hydrolyzed with dilute hydrochloric acid, and extracted with ether. The residue from the concentrated extract was treated with 85% formic acid at reflux for 2.5 hr, after which sodium hydroxide was added and the product (21 g, 0.865 mole, 86.5%) isolated from an ether extract was purified by preparative vpc (20% QF-1 on 30–60 mesh Chromosorb P).

The infrared spectrum showed significant absorptions at 3100–2860, 1590, 1570, 1490, 1470, and 1430 cm^{-1}.

The nmr spectrum showed a multiplet at 2.88 (9 H) and a singlet at 8.22 (6 H).

Anal. Calcd for $C_{16}H_{15}Cl$: C, 79.17; H, 6.23; Cl, 14.61. Found: C, 78.99; H, 6.33; Cl, 14.53.

α-(*m*-Chlorophenyl)propionitrile was prepared from *m*-chlorophenylacetonitrile (25 g, 0.165 mole) by the same procedure described for α-phenylpropionitrile. The product (20.0 g, 0.108 mole, 65.6%), bp 83–96° (0.85 mm), had an nmr spectrum which showed a singlet at 2.72 (4 H), a quartet at 6.15 (1 H, $J = 7$ cps), and a doublet at 8.42 (3 H, $J = 7$ cps).

α-(*m*-Chlorophenyl)propionic acid was prepared from the corresponding nitrile (50.6 g, 0.305 mole) by the method described for α-phenylpropionic acid. The acid product (42.1 g, 0.228 mole, 75%) had mp 68–73° (lit.[48] mp 75.5–76°).

The nmr spectrum showed a singlet at 0.2 (1 H), a multiplet at 2.8 (4 H), a quartet at 6.34 (1 H, $J = 7$ cps), and a doublet at 8.53 (3 H, $J = 7$ cps).

α-(*m*-Chlorophenyl)propiophenone was prepared in the same manner as α-phenyl-*p*-methylpropiophenone from α-(*m*-chlorophenyl)propionic acid (42.1 g, 0.228 mole) and phosphorus trichloride (12.5 g, 0.091 mole) followed by treatment of the resulting acid chloride with aluminum chloride (53.3 g, 0.4 mole) in benzene (100 ml). The product (36.2 g, 0.148 mole, 65%) had bp 140–148° (0.1 mm).

The nmr spectrum showed multiplets at 2.08 and 2.77 (9 H), a quartet at 5.41 (1 H, $J = 7$ cps), and a doublet at 8.55 (3 H, $J = 7$ cps).

2-(3-Chlorophenyl)-3-phenyl-2-butene (3c).—α-(*m*-Chlorophenyl)propiophenone (36.2 g, 0.148 mole) was slowly added to an ether solution of methylmagnesium iodide prepared from methyl iodide (31.6 g, 0.22 mole) and magnesium turnings (5.4 g, 0.22 g-atom) in diethyl ether (230 ml). After being maintained at reflux for 12 hr, the cooled solution was hydrolyzed with dilute hydrochloric acid and the aqueous solution was extracted with ether and benzene. Treatment of the crude alcohol with 85% formic acid at reflux for 2.5 hr or 20% sulfuric acid at reflux for 17.5 hr produced 2-phenyl-3-(3-chlorophenyl)-1-butene. The infrared spectrum showed significant absorptions at 1620 and 905 cm^{-1}. The nmr spectrum showed a multiplet at 2.6–7.2 (9 H), a singlet with fine structure at 4.65 (1 H) and 4.93 (1 H), a quartet at 6.1 (1 H, $J = 7$ cps) and a doublet at 8.62 (3 H, $J = 7$ cps).

Isomerization of the double bond was accomplished by treating the olefin with concentrated sulfuric acid at 25° for 30 min, followed by addition to crushed ice and extraction into ether. Two closely spaced vpc peaks were collected from an analytical column (10% Carbowax 20M on 80–100 mesh Chromosorb W) as one sample. The infrared spectrum showed absorptions at 3080–2850, 1600, 1560, 1480, 1470, and 1440. The nmr spectrum showed multiplets at 2.70 and 2.97 (9 H) and singlets at 7.84, 8.12, and 8.18 (6 H).

Anal. Calcd for $C_{16}H_{15}Cl$: C, 79.17; H, 6.23; Cl, 14.61. Found: C, 79.43; H, 6.44; Cl, 14.42.

A small sample of the major component was collected from an analytical vpc column. The nmr spectrum showed a multiplet at 2.73 (9 H), and two singlets at 8.13 and 8.20 (6 H).

Aprotic Decomposition of α-Phenylisobutyrophenone Tosylhydrazone (1a).—The procedure was patterned after reports by Smith, Shechter, Bayless, and Friedman,[7a] and Kaufman, Smith, Vander Stouw, and Shechter.[49] Sodium methoxide

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(0.432 g, 0.008 mole) was added to a solution of the tosylhydrazone (0.597 g, 0.00152 mole) in dry tetrahydrofuran (15 ml, distilled from lithium aluminum hydride) and the mixture was heated to reflux with an infrared bulb. The solution turned brick red and a copious amount of fluffy precipitate formed. The solvent was evaporated and the beige solid residue was kept under vacuum ($\leq$0.1 mm) at 25° for 3 hr. All operations were conducted in a nitrogen atmosphere. Nitrogen was bled back into the flask which was connected by means of a glass tube to a dry ice–isopropyl alcohol-cooled trap which was attached to a eudiometer tube. The dry tosylhydrazone salt was slowly (*ca.* 1 hr) heated with an oil bath to 160° at which time nitrogen ceased to evolve and the nitrogen volume produced represented 100% reaction. The dry reaction products were washed out with distilled water and extracted into ether to give an orange solution which was examined by infrared and nmr.

The reaction products could not be separated by vpc on Tide (9 ft, 30–60 mesh Chromosorb P); 5% SE-30 (5 ft, 60–80 mesh Chromosorb W; 10% diisodecylphthalate (10 ft, 70–80 mesh Chromosorb W; 5% Apiezon-L (5 ft); 10% Polar Ucon (8 ft, 60–80 mesh Chromosorb W; 15% tris(cyanoethoxy)propane (15 ft, 60–80 Chromosorb W); 6.5% E-600 (5 ft, 60–80 mesh Chromosorb P); 20% DEGS (20 ft, 60–80 mesh Chromosorb W); 20% Carbowax 20M (10 ft, 45–60 mesh Chromosorb P); 10% D. C. Silicone Grease; and activated cocoanut charcoal (4 ft, 6–14 mesh). Nmr analysis of the product mixture is described in the section on tosylhydrazone salt decomposition.

Decomposition of α-Phenylisobutyrophenone Tosylhydrazone (1a) in Ethylene Glycol.—A slurry of the tosylhydrazone (0.620 g, 0.00158 mole) in ethylene glycol (10 ml, redistilled) was stirred with sodium methoxide (0.432 g, 0.008 mole) and heated with an infrared lamp until the mixture became homogeneous. The solution was then heated in an oil bath at 161° until nitrogen evolution ceased, was cooled, then poured into 80 ml of distilled water, and extracted with ether.

The infrared spectrum from the yellow oil residue from the ether extract showed significant absorptions at 3580, 3400, 3100–2870, 1670 (w), 1600, 1490, 1450, 1370, 1100, 1050, and 1025 cm^{-1}.

The nmr spectrum showed an upfield singlet at 8.23 (product **2a**) but no absorption which corresponded to **3a** or **4a**.

Aprotic Decomposition of α-(*p*-Tolyl)isobutyrophenone Tosylhydrazone (1b).—The procedure previously described led to a mixture of compounds, the nmr analysis of which is described in the section on tosylhydrazone salt decomposition.

Decomposition of α-(*p*-Tolyl)isobutyrophenone Tosylhydrazone (1b) in Ethylene Glycol.—The solution of the salt was heated to a final temperature of 195°, cooled, and worked up in the manner previously indicated.

The infrared spectrum of the yellow oil showed absorptions at 3580, 3400, 3060–2860, 1670 (s), 1600 (w), 1580 (w), 1500, 1480, 1460, 1440, 1380, 1360, 1250, 1110, 1090, 1045, and 1018, 970, and 900 (w) cm^{-1}.

The nmr spectrum showed upfield singlets at 8.20 and 7.70 (product **2b**), but no absorptions characteristic of **3b** or **4b**.

Aprotic Decomposition of α-(*m*-Chlorophenyl)isobutyrophenone Tosylhydrazone (1c).—The dried sodium salt of the tosylhydrazone was heated to a final temperature of 195° as previously described. Analysis of the nmr spectrum is described in the section on tosylhydrazone salt decomposition.

Decomposition of α-(*m*-Chlorophenyl)isobutyrophenone Tosylhydrazone (1c) in Ethylene Glycol.—A solution of the salt was heated to a final temperature of 185° and worked up in the manner previously indicated.

The infrared spectrum of the yellow oil residue showed absorptions at 3400 (br), 3080–2870, 1670 (s), 1600, 1570, 1490 (sh), 1460, 1440, 1410, 1380, 1360, 1220, 1165, 1150, 1110, 1090, 1075, 1040, 1025 (sh), 1010 (w), 1000, 970 (s), 905, and 875 cm^{-1}. The nmr spectrum showed an upfield singlet at 8.22 (product **2c**), but no absorptions which corresponded to **3c** or **4c**.

Registry No.—**1a**, 14161-61-6; α-phenylisobutyrophenone, 13740-70-0; 4-methyldeoxybenzoin, 2430-99-1; **1b**, 14161-64-9; α-(*p*-tolyl)isobutyrophenone, 14271-33-1; **1c**, 14161-65-0; α-(*m*-chlorophenyl)isobutyrophenone, 14161-66-1; **2a**, 781-33-9; **2b**, 14161-67-2; **2c**, 14161-68-3; **3a**, 782-06-9; **3b** (*cis*), 14161-70-7; **3b** (*trans*), 14161-71-8; **3c** (*cis*), 14161-87-6; **3c** (*trans*), 14161-88-7; **4a** (*cis*), 14161-72-9; **4a** (*trans*), 14161-73-0; **4b** (*cis*), 14161-74-1; **4b** (*trans*), 14161-75-2; **5**, 14161-76-3; α-methylstilbene, 779-51-1; 1,3-diphenylbutane, 1520-44-1; 3,5-diphenyl-5-methyl-Δ^2-pyrazoline, 14161-79-6; α-phenylpropionitrile, 1823-91-2; α-phenylpropionic acid, 492-37-5; α-phenyl-*p*-methylpropiophenone, 14161-82-1; *p*-methyl-β-methylcinnamic acid, 14271-34-2; 1-benzoyl-2-(*p*-tolyl)propene, 14161-83-2; 3-phenyl-5-methyl-5-*p*-tolyl-Δ^2-pyrazoline, 14409-83-7; α-(*m*-chlorophenyl)propionitrile, 14271-35-3; α-(*m*-chlorophenyl)propionic acid, 14161-84-3; α-(*m*-chlorophenyl)propiophenone, 14161-85-4; 2-phenyl-3-(3-chlorophenyl)-1-butene, 14161-86-5.

Cycloadditions. XV. The Mercury-Sensitized Gas Phase Photodecarbonylation of Norcamphor[1,2]

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The mercury-sensitized gas phase photodecarbonylation of norcamphor gave as primary products 1,5-hexadiene and bicyclo[2.1.1]hexane. In important secondary photochemical reactions, 1,5-hexadiene was converted into bicyclo[2.1.1]hexane and allylcyclopropane. Concentration *vs.* time data for norcamphor, carbon monoxide, and these three hydrocarbons provided the distinctions between primary and secondary processes; the experimental curves were well-matched by plots generated by an analog computor programmed for an appropriate mechanistic scheme. Photolysis of bicyclo[2.1.1]hexane did not give substantial amounts of isomeric hydrocarbons. Photolysis of (2-cyclopentenyl)ethanal gave cyclohexene as the major product.

Although the direct, unsensitized photodecarbonylation of norcamphor in the gas phase gives 1,5-hexadiene and bicyclo[2.1.1]hexane,[5] the mercury-sensitized gas phase photodecarbonylation has been reported[6] to give at least three *primary* products, 1,5-hexadiene, bicyclo[2.1.1]hexane, and allylcyclopropane. The formation of allylcyclopropane from norcamphor in a primary process has been repeatedly cited in the re-

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(3) Alfred P. Sloan Research Fellow.

(4) Eli Lilly and Company Fellow, 1964-1965; Allied Chemical Fellow, 1965–1966; Standard Oil of California Fellow, 1966–1967.

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