ESTER HYDRAZONES AS POSSIBLE PRECURSORS TO ALKOXYDIAZOALKANES[1]

II. THE DECOMPOSITION OF ESTER (*p*-TOLYLSULFONYL)HYDRAZONE SALTS IN APROTIC SOLVENTS

Robert J. Crawford and Rintje Raap[2]
Department of Chemistry, University of Alberta, Edmonton, Alberta

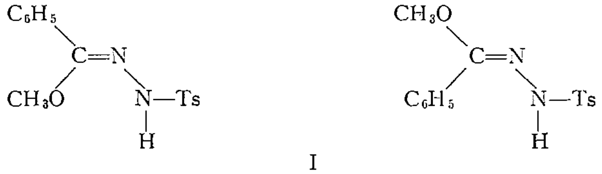
Received July 10, 1964

ABSTRACT

The thermal and photochemical decomposition of methyl benzoate (*p*-tolylsulfonyl)hydrazone salts in 1,2-dimethoxyethane, 1,2-diethoxyethane, or diglyme gives rise to benzaldehyde dimethyl acetal, methyl benzoate azine (II), *meso*-1,2-diphenyl-1,2-dimethoxyethane, and methyl α-(*p*-tolylsulfonyl)benzyl ether. The thermal decomposition in the presence of diethyl fumarate produced diethyl 3-methoxy-3-phenyl-*trans*-1,2-cyclopropanedicarboxylate (XIV) in 62% yield; a low yield (4%) of the two isomeric forms of 1-methoxy-2-*n*-octyl-1-phenylcyclopropane (V) was formed in 1-decene. The thermal and photochemical decomposition of potassium 4-pentenyl benzoate (*p*-tolylsulfonyl)hydrazone (XVIII) produced 1-phenyl-2-oxabicyclo[4.1.0]heptane (XXI) in 14 and 21% yield respectively. These products provide additional evidence for the occurrence of alkoxydiazoalkanes and suggest alkoxycarbenes as possible intermediates in the decomposition of ester (*p*-tolylsulfonyl)hydrazone salts.

INTRODUCTION

Diazoalkanes undergo thermal and photochemical decomposition in aprotic solvents to give rise to a number of unique products (1). The reactions of the sodium salts of I in protic solvents was shown, in the preceding paper (2), to decompose in a manner reconcilable with an alkoxydiazoalkane intermediate. We have herein undertaken a study of the decomposition of the sodium salts of I in aprotic solvents in an attempt to gain information of a synthetic and mechanistic value.


I

DISCUSSION*

The sodium salt of I was prepared by dissolving the hydrazone I in DME with an equimolar amount of sodium methoxide. The methanol was distilled off and the resulting solution refluxed for 65 h, as judged sufficient by the decreased rate of nitrogen evolution. The products were benzaldehyde dimethyl acetal (34%) and a solid, m.p. 72–73°, that was isolated by chromatography, on alumina, of the nonvolatile fraction. The infrared spectrum of the solid showed an intense absorption at 1 615 cm^{-1}, indicative of C=N. The nuclear magnetic resonance (n.m.r.) spectrum indicated aromatic protons at τ 2.0 to 2.8 and a sharp $-OCH_3$ singlet at τ 6.18, with relative areas of 10:6 respectively. The compound has a molecular weight of 269 and its elemental composition fits the empirical formula

---

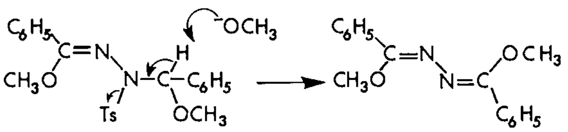
[1] *Presented at the 47th Canadian Chemical Conference, Kingston, Ontario, June 1–3, 1964.*

[2] *Holder of a National Research Council of Canada Scholarship, 1963–1964. Present address: R & L Molecular Research Ltd., Edmonton, Alberta.*

**Solvents such as 1,2-dimethoxyethane(DME), 1,2-diethoxyethane (DEE), and diglyme were freed, prior to use, from hydroxylic materials by distillation from potassium metal.*

Canadian Journal of Chemistry. Volume 43 (1965)

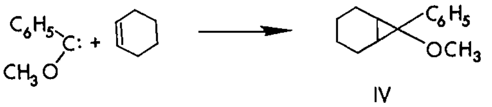
$C_{16}H_{16}N_2O_2$ (molecular weight 268.3). There is little doubt that the product is methyl benzoate azine (II), as the same product was prepared from methyl benzoate (α-methoxybenzyl)(*p*-tolylsulfony)hydrazone (III) (2) by refluxing with sodium methoxide in DME.



III II

An n.m.r. spectrum of the product mixture resulting from the decomposition of the potassium salt of I indicated that, apart from benzaldehyde dimethyl acetal and methyl benzoate azine (II), other products were present containing only aromatic hydrogens. Possible products such as benzonitrile, diphenylacetylene, and biphenyl could not be detected by infrared spectroscopy and (or) gas-liquid partition chromatography (g.l.p.c.), neither could any other product be isolated by elution chromatography on alumina.

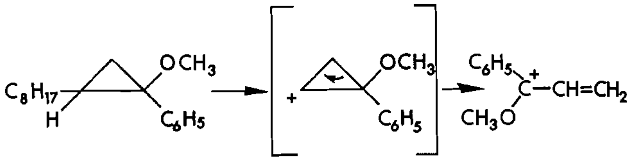
When the decomposition was repeated in the presence of cyclohexene the product mixture was the same as that obtained in the absence of cyclohexene and there was no indication of the formation of 7-methoxy-7-phenylnorcarane (IV), which would have resulted from a reaction between phenylmethoxycarbene, a possible decomposition intermediate, and cyclohexene.



IV

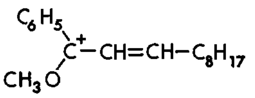
The potassium salt, when heated alone in diglyme, dissolved at the boiling point, and was completely decomposed within 5 min. Benzaldehyde dimethyl acetal, although not isolated, was shown to be present by g.l.p.c. A very complicated product mixture had resulted from this decomposition as was indicated by n.m.r. spectroscopy, and only two products were isolated in small amounts, methyl benzoate azine (II) (2.5%) and *meso*-1,2-diphenyl-1,2-dimethyoxyethane (3%). That the solvent was not involved in the formation of the benzaldehyde dimethyl acetal was shown by the isolation of this product, in 30% yield, from the thermal decomposition of the potassium salt in DEE.

A further attempt to isolate a cyclopropane derivative was made by carrying out the decomposition in 1-decene. The boiling point of this olefin (168°) is such that it may be used as a 1:1 mixture with diglyme. The reaction product obtained when the potassium salt was decomposed at 158° had a n.m.r. spectrum very similar to that of the product that was obtained when the decomposition was carried out in diglyme alone. However, when the product mixture was repeatedly chromatographed on alumina, a 2.2% yield of a pure liquid was obtained. The molecular weight of the compound was found to be 260; this, together with an elemental analysis, established the empirical formula as $C_{18}H_{28}O$ (molecular weight 260.4). The infrared spectrum showed a weak band at 1 020 cm^{-1}, a position corresponding to a cyclopropane ring deformation frequency (3) and strong absorption in the region 1 050 to 1 080 cm^{-1}, indicative of an ether linkage. The n.m.r. spectrum contains singlets at τ 2.81 and 6.84 and a broad band at τ 8.3–9.4 (with a strong maximum at 8.72 and a weak maximum at 9.11) with relative areas 1.8:1.0:10.4. These findings led to the conclusion that the compound was indeed one of the isomers of the desired cyclopropyl derivatives V. The mass spectrum provides further evidence as the major fragment, accounting for 13.8% of the fragmentation products, has a *m/e* = 147, which corresponds with the carbonium ion VI whose presence may arise by the following sequence:

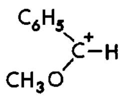


V VI

The fragment with *m/e* = 259 can similarly be explained by the initial loss of hydrogen, instead of the octyl group, to give the carbonium ion VII. The second largest fragment (6.8%), *m/e* = 121, is believed to be α-methoxybenzyl carbonium ion (VIII).

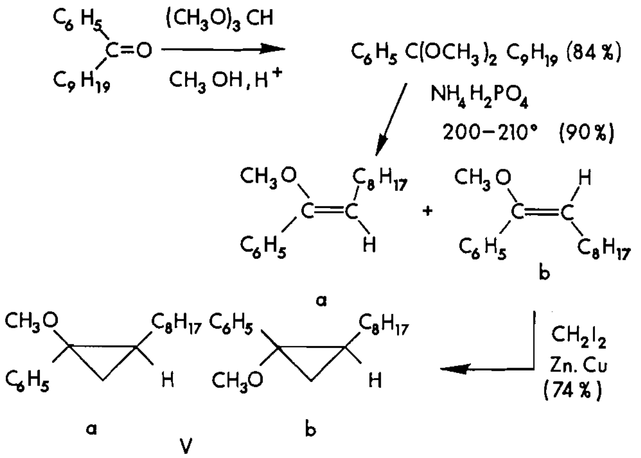


VII



VIII

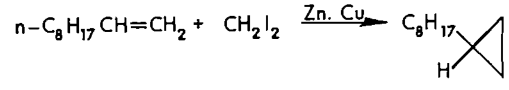
The configuration assignment of the isolated isomer, and the detection of the other isomer, required the synthesis of the isomers V*a* and V*b*. The mode by which this synthesis was accomplished is outlined in reaction Scheme 1, in which the yields of the individual steps are also indicated.



SCHEME 1

When the Simmons–Smith reaction (4) was carried out with the mixture of isomers of IX, a 5:3 mixture of the cyclopropyl isomers of V was obtained. The n.m.r. spectrum showed that the principal product has the same signal pattern as that isolated from the thermal decomposition of the potassium salt of I in the presence of 1-decene. The aromatic protons and the methoxy group appear in V*b* as singlets at τ 2.73 and 6.98 respectively, whereas the octyl group appears as a broad band at τ 8.6–9.2, with a strong maximum at

8.83 and a smaller maximum at τ 9.04. The position of the octyl group in the n.m.r. spectrum may serve as a means for the configuration assignment. The n.m.r. spectra displayed a distinct difference in the position of the two maxima of the octyl group in the two isomers. It was felt that, due to steric and electronic interactions, the proximity of a phenyl group to the octyl group, as in V*b* and IX*b*, would alter the position of the latter more than the *cis*-methoxy group would in structures V*a* and IX*a*. Thus the octyl maxima in V*a* and IX*a* were expected to be very much the same as in the unsubstituted *n*-octylcyclopropane (X).

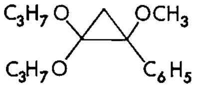


X

The n.m.r. spectrum of X shows the two octyl maxima at τ 8.78 and 9.11. As these maxima appear at the same positions in the principal product from either the dealcoholation or the methylene-transfer reaction, there is little doubt that they can also be attributed to the favored reaction products IX*a* and V*a*.

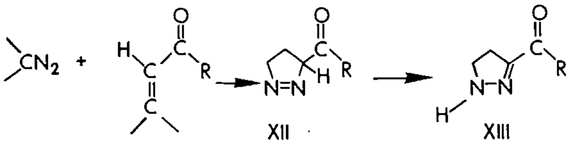
With the configurations established, it was thus possible to determine the isomeric ratio of the cyclopropanes that resulted from the thermal decomposition in 1-decene at 155–165°. The yield of 1-methoxy-2-*n*-octyl-1-phenylcyclopropane (V), determined by g.l.p.c.,* amounted to 4%; the relative ratio of V*a* and V*b* was 1.8:1 respectively.

It was thought that a more electron-rich olefin would give a better yield of cyclopropane derivative. Ketene diethylacetal has been shown to act as a very efficient carbene trap (5) and thus ketene dipropyl acetal, with a boiling point of 153°, was most suitable for the present purpose. No 1-methoxy-2,2-di-*n*-propyloxy-1-phenylcyclopropane (XI) could be isolated from the complex product mixture that was obtained when the potassium salt of I was decomposed at 150–155° in a 1:1 mixture of diglyme and ketene dipropyl acetal. Although the n.m.r. spectrum of a distillation fraction boiling at 90–125° (0.2 mm) showed a complicated signal pattern at τ 8.3–9.5, which could only be due to propyl groups, no separation could be effected by elution chromatography on alumina. However it could be concluded from the n.m.r. spectrum that compound XI is certainly not formed in a yield exceeding 4%, and therefore the use of a ketene acetal does not seem to have much effect on the yield of the carbene adduct.



XI

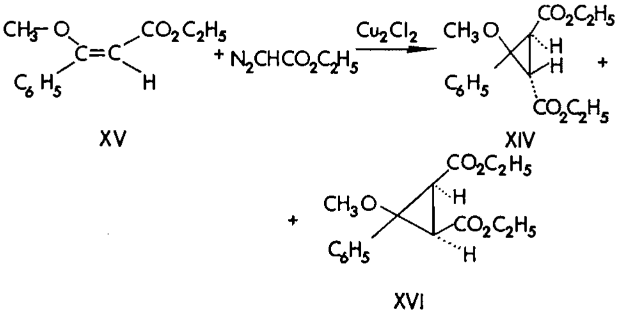
Diazo compounds and olefins, e.g. α,β-unsaturated carbonyl compounds, react to produce 1-pyrazolines (XII) which generally rapidly isomerize to 2-pyrazolines (XIII) and in certain instances decompose to cyclopropane derivatives (6).



---

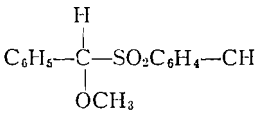
*A 4 ft Apiezon M column at 220° was used. It was shown that the product did not isomerize on the column, as an analysis of an authentic mixture of Va and Vb by g.l.p.c. and by n.m.r. spectroscopy gave the same result.

The formation of a pyrazoline from the decomposition of the potassium salt of I in the presence of an α,β-unsaturated carbonyl compound would provide additional evidence for the existence of the intermediate phenylmethoxydiazomethane. The potassium salt of I was decomposed at 130–135° in diethyl fumarate. A solid was isolated in 62% yield, by elution chromatography on alumina, m.p 40–41°. The infrared spectrum of the product showed an intense absorption in the carbonyl region at 1 720 cm^{-1}. The n.m.r. spectrum contained singlets at τ 2.77, 6.98, and 7.14, two methylene quartets (J = 7 c.p.s.) of the same intensity at 5.82 and 6.17, and two methyl triplets (J = 7 c.p.s.) of the same intensity at τ 8.69 and 9.02, the approximate relative areas were respectively 5:3:2:4:6. As the product did not contain any nitrogen and the infrared and n.m.r. spectra did not indicate the presence of an olefinic double bond or olefinic hydrogens, its structure was believed to be that of diethyl 3-methoxy-3-phenyl-*trans*-1,2-cyclopropanedicarboxylate (XIV), a conclusion in agreement with the elemental analysis. However a less ambiguous proof of structure appeared necessary, and therefore the cyclopropane derivative XIV was synthesized as shown in Scheme 2. Ethyl *trans*-β-methoxy cinnamate (XV), prepared by the procedure of Arndt and Loewe (7) for the methyl ester, was allowed to react with carbethoxycarbene, generated from ethyl diazoacetate under the catalytic influence of cuprous chloride. Diethyl 3-methoxy-3-phenyl-*trans*-1,2-cyclopropanedicarboxylate (XIV) and diethyl 3-methoxy-*trans*-3-phenyl-*cis*-1,2-cyclopropanedicarboxylate (XVI) were obtained in yields of 10% and 3% respectively. Compound XIV was identical in all respects with the solid obtained from the thermal decomposition of the potassium salt of I in diethyl fumarate.



SCHEME 2

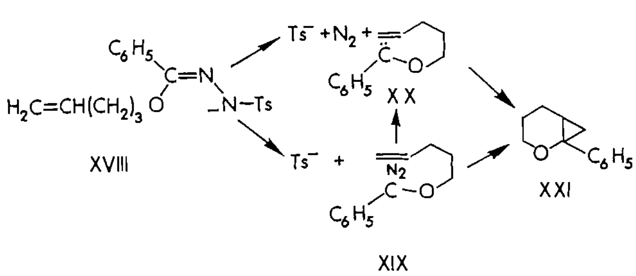
The photochemical decomposition of the potassium salt of I at room temperature in a 1:1 mixture of DME and cyclohexene was also investigated. Prior to the work-up the presence of a trace of methanol was demonstrated by g.l.p.c. Benzaldehyde dimethyl acetal was again isolated (36%), and treatment of the product mixture with *n*-hexane caused a solid to precipitate that was obtained as white needles, m.p. 101–103° (decomp.). The infrared spectrum showed strong absorption at 1 128 cm^{-1} and in the region 1 290 to 1 320 cm^{-1}, suggesting the presence of a sulfone group (7). The n.m.r. spectrum showed aromatic proton signals in the region τ 2.4–2.9, with a sharp singlet at 2.73, and further singlets at 4.82, 6.35, and 7.62, with integrated areas 9:1:3:3. The compound was found to have a molecular weight of 272 and to fit the emperical formula $C_{15}H_{16}O_3S$ (molecular weight 276.3). From this it is clear that the product is methyl α-(*p*-tolylsulfonyl)benzyl ether (XVII). This product was isolated in 3.2% yield; however, it could be isolated in as high as a 17% yield when the photochemical decomposition was carried out in DME alone. Although a large number of other products were produced, as demonstrated both by n.m.r. spectroscopy and g.l.p.c., they could not be isolated in pure form by distillation and (or) elution chromatography.



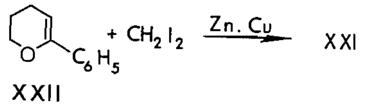
$$C_6H_5-\overset{H}{\underset{OCH_3}{C}}-SO_2C_6H_4-CH_3$$

XVII

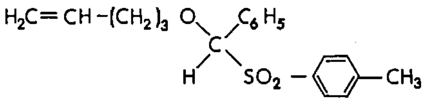
Since the phenylmethoxydiazomethane gave such such poor yields of cyclopropane products with 1-decene, it was decided to investigate the efficiency of an internally situated olefinic double bond to cyclopropane formation. Because of the availability of 4-pentenol the corresponding potassium 4-pentenol benzoate (*p*-tolylsulfonyl)hydrazone (XVIII) was prepared and reactions of it studied. Thus if cyclopropane ring formation occurred through the diazoalkane (XIX) or the carbene (XX), the olefinic double bond would be suitably disposed to trap the intermediate and lead to the formation of 1-phenyl-2-oxabicyclo[4.1.0.]heptane (XXI).



In order to facilitate the isolation and quantitative determination of XXI it was first synthesized by a Simmons–Smith reaction on 2-phenyl-2-dihydropyran (XXII) in 72% yield. The infrared spectrum of the product shows an absorption of medium intensity at 1 024 cm^{-1}, characteristic of a cyclopropyl group (3). The n.m.r. spectrum contains a singlet at τ 2.09 and complex absorption at τ 6.1–7.0 and 7.8–9.2, with relative areas 5:2:7 respectively.



The thermal decomposition of XVIII was carried out in diglyme at 140–150°, at which temperature the salt readily decomposed. The amount of XXI in the product mixture was quantitatively determined by g.l.p.c. To establish its identity it was also isolated by elution chromatography. The pyran (XXI) was the major product in the thermal decomposition, its yield amounting to 11–14%. Although several modifications in the decomposition procedure were investigated in order to improve this yield, they were without success. When a dilute solution of XVIII in anhydrous diethyl ether was photolyzed at room temperature, the product XXI was formed in 20–21% yield. The photochemical decomposition also produced an appreciable amount (15%) of 4-pentenyl α-(*p*-tolylsulfonyl)benzyl ether (XXIII), as a white crystalline solid, m.p. 90–91°.



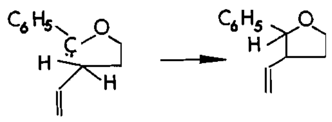
XXIII

The presence of another expected product, benzaldehyde 4-pentenyl acetal (XXIV), was shown by g.l.p.c. and its yield was estimated at 3–6% from the thermal decomposition and 1–4% in the photochemical decomposition. As this low yield did not permit an effective isolation it was only characterized by its retention time on an Apiezon M column. Authentic benzaldehyde 4-pentenyl acetal was prepared in 80% yield by the thermal decomposition of XVIII in DEE in the presence of 4-pentenol.

$$C_6H_5CH(O(CH_2)_3CH{=}CH_2)_2$$

XXIV

The possibility of carbene insertion into the allylic 3-position of the alkyl group in XVIII to form the vinyl furan (XXV) was seriously considered since the vapor phase chromatogram, of the product mixture from the decomposition of XVIII, displayed a relatively large amount (estimated at 3 to 4% in the thermal and at 5 to 7% in the photochemical decomposition) of a product with a similar retention time to that of XXI. However it was later found that this product resulted from the thermal decomposition of the sulfone XXIII, and the idea was abandoned as the chromatogram indicated that the insertion product XXV had not been formed, if at all, in a yield greater than 1%.



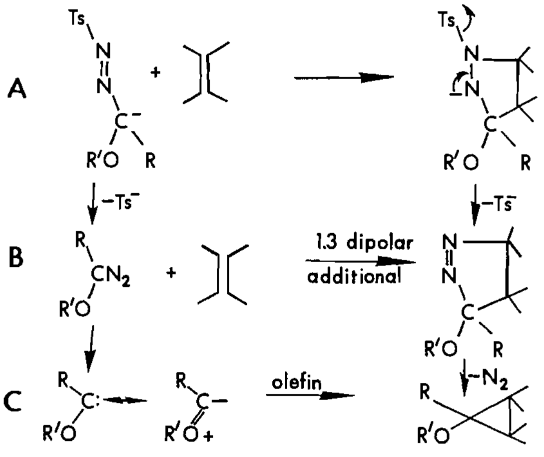
XXV

CONCLUSIONS

The production of benzaldehyde dimethylacetal in aprotic solution along with the formation of methanol suggests that the salts are decomposing by routes as yet not elucidated. The methanol formed in this process would appear to occur via alkoxy radicals abstracting from the solvent, since the methanol can be detected by g.l.p.c. on the anhydrous solutions before work-up.

Three possible reaction paths which may explain the cyclopropane formation with 1-decene and diethyl fumarate, are shown in Scheme 3.

Mechanism A involves a nucleophilic attack on the olefin which although reasonable for diethyl fumarate, seems less likely for 1-decene. Mechanism B involves a 1,3-dipolar addition of the diazocompound to the olefin, but requires that the loss of nitrogen be more rapid than the rate of tautomerization of 1-pyrazoline (6). Mechanism C involves the thermal decomposition of the alkoxydiazoalkane to an alkoxy carbene which may have nucleophilic properties similar to the carbene species investigated by Wanzlick (9) and Kirmse (10). Thus diethyl fumarate is a superior trap to any of the other olefins. It is not possible on the basis of existing data to discriminate among these three mechanisms, and minor variations thereof, but since phenyldiazomethane can be prepared, and isolated, by



SCHEME 3

this method and since nucleophilic addition to 1-decene does not seem likely,* mechanisms B and C are favored.

EXPERIMENTAL

All melting points and boiling points are uncorrected.

The infrared spectra were obtained on a Perkin–Elmer Model 421 spectrophotometer equipped with grating optics. Nuclear magnetic resonance spectra were measured using a Varian Associates Model A-60 spectrometer, with tetramethylsilane as a reference. Ultraviolet spectra were obtained using a Cary Model 14M recording spectrophotometer. Mass spectra were obtained on a A.E.I. MS2-H mass spectrometer.

Vapor phase chromatography was carried out with a Perkin–Elmer Model 154 vapor fractometer or a F. & M. Model 500 temperature-programmed gas chromatograph.

The photochemical decompositions were all carried out in a quartz reaction vessel, cooled by running tap water, with an internally situated 250 W Hanovia ultraviolet source.

The microanalyses were performed by Pascher Mikroanalytisches Laboratorium (Bonn, West Germany), Daessle Organic Microanalyses (Montreal), and the Microanalytical Laboratory of the Department of Chemistry, University of Alberta (Edmonton).

The Decompositon of α-Alkoxy(p-tolylsulfonyl)hydrazone Salts

Solvents

1,2-Dimethoxyethane was distilled from potassium metal, b.p. 82°. A technical grade of *1,2-diethoxyethane* was distilled. The fraction boiling at 116–120° was left with potassium overnight and fractionally distilled. The fraction with b.p. 116–117° consisted of pure 1,2-diethoxyethane as was shown by g.l.p.c. *Diglyme* (diethylene glycol dimethyl ether) was left over potassium metal overnight and distilled, b.p. 157–159°.

The Thermal Decomposition of Sodium Methyl Benzoate (p-Tolylsulfonyl)hydrazone in 1,2-Dimethoxyethane

Methyl benzoate (*p*-tolylsulfonyl)hydrazone (10.0 g, 32.9 mmole) (1) was dissolved in 60 ml of 1,2-dimethoxyethane, and sodium methoxide (1.8 g, 33.3 mmole) was added. Solvent was distilled (approximately 20 ml) until the boiling point reached that of pure 1,2-dimethoxyethane. The mixture was stirred and refluxed for 65 h. After cooling, the sodium *p*-toluenesulfinate (5.3 g, 90%) was filtered off and the solvent of the orange-colored solution was removed. The residue was dissolved in ether, washed with water, and dried. Removal of the ether gave 3.1 g liquid residue. A vacuum distillation produced 0.9 g (34%) benzaldehyde dimethyl acetal, b.p. 56–57° (3.5 mm); n_D^{25} 1.4960. The high-boiling point liquid residue was chromatographed on Harshaw alumina. The product obtained by elution with a 5% ether in pentane solution was recrystallized from a small amount of *n*-hexane to give 0.5 g (12%) of methyl benzoate azine (II) as white needles, m.p. 72–73°. The ultraviolet spectrum shows a broad band with a maximum at 2 700 Å (log = 4.09).

Anal. Calcd. for $C_{16}H_{16}N_2O_2$ (molecular weight, 268.3); C, 71.62; H, 6.01; N, 10.44. Found: C, 71.87; H, 5.99; N, 10.49; molecular weight (osmometric), 269.

Although other products were formed that contained only aromatic protons, as was shown by n.m.r. spectroscopy, no other compounds could be isolated and characterized. When the experiment was repeated

---

**The rate of nitrogen evolution appears to be independent of the presence of the olefin substrate which would not seem reasonable for mechanism A.*

in the presence of 15 ml cyclohexene, the same product mixture was obtained and there was no indication for the formation of 7-methoxy-7-phenylnorcarane as the n.m.r. spectrum of the reaction products showed no absorption above 7.0.

The Reaction of Methyl Benzoate (α-Methoxybenzyl)(p-tolylsulfonyl)hydrazone with Sodium Methoxide

Methyl benzoate (α-methoxybenzyl)(*p*-tolylsulfonyl)hydrazone (0.500 g, 1.18 mmole) (2) and sodium methoxide (0.072 g, 1.33 mmole) were refluxed in 20 ml of 1,2-dimethoxyethane. A precipitate formed slowly and after 5.5 h the mixture was cooled and sodium *p*-toluenesulfinate (0.16 g, 76%) was filtered off. The solvent was removed and the residue was dissolved in ether, washed with water, and dried. Removal of the ether produced 0.33 g of residue that slowly solidified. An infrared spectrum was identical with that of a mixture of starting material and methyl benzoate azine. Addition of *n*-hexane caused the starting material (0.08 g, 16%) to precipitate. The remaining product was chromatographed on alumina. The pure azine was obtained by elution with a 5% ether in pentane solution and amounted to 0.14 g (46%), m.p. 72–73°; mixture m.p. 72–73°.

The Thermal Decomposition of Potassium Methyl Benzoate (p-Tolylsulfonyl)hydrazone in 1-Decene

A suspension of the potassium salt (1.50 g, 4.4 mmole) in 15 ml of 1-decene was heated, while being stirred, at 155–165° until the gas evolution had ceased, which required approximately 40 min. The reaction mixture was cooled and water and diethyl ether were added. The organic layer was dried, and the ether and 1-decene distilled off, the latter under reduced pressure. It was shown by g.l.p.c. that the residue contained at least 13 different products, all present in relatively low concentrations. In order to be able to analyze for the two isomeric 1-methoxy-2-*n*-octyl-1-phenylcyclopropanes (V), the mixture was added to an alumina column and eluted with *n*-pentane until all of the desired product was removed from the column. This operation required approximately 700 ml of *n*-pentane. The pentane was removed and an accurately known amount of 2-ethoxynaphthalene was added as an internal standard. The total amount of 1-methoxy-*trans*-2-*n*-octyl-1-phenylcyclopropane and 1-methoxy-*cis*-2-*n*-octyl-1-phenylcyclopropane was determined by g.l.p.c. using a 4 ft Apiezon M column. In two separate experiments the total amount of these two isomers was 47 mg (4.1%) and 42 mg (3.8%). the isomer ratio *trans*/*cis* being 1.9 and 1.7 respectively. It was shown that the product did not isomerize at the column temperature (220°) as the analysis of an authentic mixture of the two isomers by n.m.r. spectroscopy and by g.l.p.c. gave the same result.

The decomposition was repeated on a larger scale in a 1:1 mixture of diglyme and 1-decene: The potassium salt (10.0 g, 29.2 mmole) was decomposed by refluxing for 10 min in a mixture of 30 ml diglyme and 30 ml 1-decene. Prior to the work-up an appreciable amount of benzaldehyde dimethyl acetal was shown to be present in the reaction mixture by g.l.p.c. on an Apiezon L column. A quantitative amount of potassium *p*-toluenesulfinate was filtered off and the solvent mixture was distilled off under reduced pressure. The highly colored residue was passed through a short alumina column with 300 ml of *n*-pentane. The pentane was removed and the residue distilled *in vacuo*. After a small amount of a low-boiling fraction, which was not further investigated, 1.35 g of a fraction with a boiling range of 110–140° (0.3 mm) distilled over. Upon addition of a small amount of *n*-hexane and cooling overnight at −15°, 0.1 g (3%) of crystals with m.p. 138–140° were obtained, identical in all respects (mixture melting point, infrared and n.m.r. spectra) with *meso*-1,2-diphenyl-1,2-dimethoxyethane. The hexane solution was chromatographed on alumina. The product that was eluted with a 5% ether in pentane solution was recrystallized from a small amount of *n*-hexane to give 0.1 g (2.6%) of methyl benzoate azine. The *n*-pentane fraction contained 1-methoxy-2-*n*-octyl-1-phenylcyclopropane. The product mixture from this fraction was again chromatographed on alumina and eluted with *n*-pentane. The first fraction contained 0.17 g (2.2%) of pure 1-methoxy-*trans*-2-*n*-octyl-1-phenylcyclopropane.

Anal. Calcd. for $C_{18}H_{28}O$ (molecular weight, 260.4): C, 83.02; H, 10.84. Found: C, 83.21; H, 11.11; molecular weight 260 (mass spectrometrically).

The following chromatographic fractions contained smaller amounts of a mixture of the two isomers and also other products.

The Photochemical Decomposition of Potassium Methyl Benzoate (p-Tolylsulfonyl)hydrazone in 1,2-Dimethoxyethane and Cyclohexene

A stirred suspension of the potassium salt (10.0 g, 29.2 mmole) in a mixture of 90 ml 1,2-dimethoxyethane and 100 ml cyclohexene was irradiated for 9 h, at which time the gas evolution had become almost negligible. A total of 570 ml of gas had evolved (theoretically 770 ml of nitrogen). The solution was filtered, the solvent removed under reduced pressure, and the residue taken up in ether. The ether solution was washed with water and dried and the ether removed. A n.m.r spectrum showed the residue was a mixture of many products. Addition of a small amount of *n*-hexane caused 0.26 g of a white solid to precipitate, that could be recrystallized from a 5:1 mixture of *n*-hexane and benzene to give white needles, m.p. 101–103°. Because of decomposition no sharp melting point could be obtained.

Anal. Calcd. for methyl α-(*p*-tolylsulfonyl)benzyl ether (XVII), $C_{15}H_{16}O_3S$ (molecular weight 276): C, 65.19; H, 6.83; S, 11.61. Found: C, 65.34; H, 6.29; S, 11.45; molecular weight (osmometric) 272, 274.

The *n*-hexane was removed and the residue distilled *in vacuo* to give 0.8 g (36%) benzaldehyde dimethyl acetal (b.p. 58–59° at 3.6 mm), 0.9 g of a fraction with b.p. 102–109° (1.0 mm), and 0.55 g of a fraction boiling at 110–116° (0.15 mm). Both these last fractions showed a very complicated n.m.r. signal pattern. An attempt was made to separate the fraction with b.p. 102–109° (1.0 mm) into its components by elution chromatography on alumina, however no separation could be effected and each fraction that was eluted from the column contained several components as was shown by n.m.r. spectroscopy and g.l.p.c.

When the photochemical decomposition was carried out in 1,2-dimethoxyethane alone, methyl α-(*p*-tolylsulfonyl)benzyl ether was isolated in 17% yield. Prior to the work-up benzaldehyde dimethyl acetal was shown to be present by g.l.p.c., using a 2 m Apiezon L column. A trace of methanol could also be detected. It was characterized by its retention time on two columns, packed with Apiezon L, and Ucon LB-550-X respectively.

The Decomposition of Potassium Methyl Benzoate (p-Tolylsulfonyl)hydrazone in Diethyl Fumarate

The potassium salt (4.0 g, 11.7 mmole) was suspended in 40 ml of diethyl fumarate (a center distillation cut, b.p. 66–67° at 1.8 mm, of Eastman white label material) and heated, while stirred, at 130–135° for 1.5 h. The mixture was cooled, 100 ml ether added, and the ether solution washed four times with water. The pale yellow-colored ether solution was dried, the ether evaporated, and the diethyl fumarate distilled off *in vacuo*. Upon addition of a small amount of *n*-pentane to the residue, methyl benzoate (α-methoxybenzyl)(*p*-tolylsulfonyl)hydrazone (III) (0.43 g, 18%; m.p. 147–149°) precipitated. The pentane was removed and the residue purified by elution chromatography on alumina. Elution with benzene produced 2.15 g of an oil that slowly solidified to a white solid, m.p. 37–39°. The product was twice recrystallized from a small amount of *n*-hexane to give fine white needles, m.p. 40–41°, of analytical purity. The melting point was not depressed by diethyl 3-methoxy-3-phenyl-*trans*-1,2-cyclopropanedicarboxylate. The infrared and n.m.r. spectra were identical with those of an authentic sample of diethyl 3-methoxy-3-phenyl-*trans*-1,2-cyclopropane dicarboxylate. No other reaction products were detected either by n.m.r. spectroscopy or elution chromatography.

4-Pentenyl Benzimidate

Dry hydrogen chloride (25.5 g, 0.70 mole) was added to a mixture of 4-pentenol (60.0 g, 0.70 mole) and benzonitrile (68.0 g, 0.66 mole) and cooled in an ice–salt mixture. The reaction mixture was left in the refrigerator for 24 h, at which time it had almost solidified, and 200 ml of ether was added. The hydrochloride salt was collected and mounted to 77.7 g (0.36 mole, 52%), m.p. 122–123° (decomp.). Under vigorous stirring this salt was added to a solution of potassium carbonate (120 g 0.87 mole) in 300 ml of water covered with 150 ml of ether, followed by the further extraction of the aqueous layer with 60 ml of ether. The combined ether solutions were dried and the residue was distilled *in vacuo* to give 59.8 g (92%) of colorless product, b.p. 86–87° (0.3 mm); n_D^{25} 1.5252. The infrared spectrum (in CCl_4) shows an N—H band at 3 340 cm^{-1} and a strong band at 1 630 cm^{-1} due to the C═N.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.41; H, 8.12; N, 7.38.

4-Pentenyl Benzoate (p-Tolylsulfonyl)hydrazone

A solution of 4-pentenyl benzimidate (15.9 g, 84.1 mmole) in 35 ml of absolute ethanol was added to a cold suspension of (*p*-tolylsulfonyl)hydrazide hydrochloride (18.7 g, 84.0 mmole) in 75 ml of absolute ethanol and the mixture was left at room temperature for 3 h. The ammonium chloride was filtered off, the ethanol removed under reduced pressure, and the residue dissolved in 120 ml of methylene chloride. The methylene chloride solution was washed twice with water, dried ($MgSO_4$), and filtered, and the solvent removed. The residue was immediately dissolved in 100 ml of anhydrous diethyl ether and cooled at −15° overnight to yield 14.4 g (48%) of crystals, m.p. 87–89°. One additional recrystallization produced an analytical sample, m.p. 89–90°. The infrared spectrum (in $CHCl_3$) shows N—H stretching at 3 300 cm^{-1} and a C═N— stretching band of medium intensity at 1 620 cm^{-1} with a shoulder at 1 635 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2O_3S$: C, 63.66; H, 6.19; N, 7.82; S, 8.95. Found: C, 63.75; H, 6.38; N, 7.68; S, 8.81.

Potassium 4-Pentenyl Benzoate (p-Tolylsulfonyl)hydrazone (XVIII)

A solution of 4-pentenyl benzoate (*p*-tolylsulfonyl)hydrazone (10.0 g, 27.9 mmole) in 40 ml of 1,2-dimethoxyethane was added to a solution of potassium (1.1 g, 28.2 mgram-atom) in a mixture of 6 ml absolute ethanol and 40 ml of 1,2-dimethoxyethane. Cooling and the addition of *n*-pentane did not cause any salt to precipitate. Thus the solvent was removed and the residue kept *in vacuo* for 30 min, at which time the syrup had crystallized completely. The slightly yellow-colored salt, soluble in water and in most organic solvents, amounted to 11.0 g.

Benzaldehyde Di-(4-pentenyl) Acetal XXIV

Potassium 4-pentenyl benzoate (*p*-tolylsulfonyl)hydrazone (11.0 g, 27.7 mmole) was refluxed in a mixture of 10 ml 4-pentenol and 40 ml of 1,2-diethoxyethane for 3 h. Potassium *p*-toluenesulfinate (5.5 g, 100%) was filtered off, the solvent removed under reduced pressure, and the residue taken up in ether, washed with water, and dried ($MgSO_4$). Removal of the solvent, followed by a vacuum distillation, yielded 5.8 g (80%) of the product, b.p. 102–103° (0.2 mm); n_D^{25} 1.4905. The infrared spectrum shows the olefinic double bond stretching as a band of medium intensity at 1 637 cm^{-1}.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.47; H, 9.19.

The Thermal Decomposition of Potassium 4-Pentenyl Benzoate (p-Tolylsulfonyl)hydrazone in Diglyme to Produce XXI

The potassium salt (1.31 g, 3.3 mmole) was dissolved in 20 ml diglyme and heated for 10 min at 145–150°. After cooling there was added 50 ml water and 75 ml *n*-pentane and the mixture was vigorously shaken. The pentane layer was again washed with water and then dried. The pentane was removed, 0.091 g of 2-ethoxynaphthalene was added as an internal standard, and the absolute amount of 1-phenyl-2-oxabicyclo[4.1.0]heptane (XXI) was determined by g.l.p.c. using a 4 ft Apiezon M column, yield 0.071 g (12.3%). The experiment was repeated, with the potassium salt slowly added, either as the solid or as a diglyme solution, to diglyme at 140–150°. The yield of XXI was 13.7% and 10.8% in two separate experiments. By carrying out the experiment on a somewhat larger scale and by eluting the product mixture with *n*-pentane from an alumina column, a pure sample of XXI could be isolated (even though the overall separation was poor) and characterized by its retention time and by comparing its infrared and n.m.r. spectra with those of an authentic sample.

The Photochemical Decomposition of Potassium 4-Pentenyl Benzoate (p-Tolylsulfonyl)hydrazone in Diethyl Ether

The potassium salt (1.571 g, 4.0 mmole) was dissolved in 190 ml of diethyl ether and irradiated for 45 min, at which time the gas evolution had ceased. The ether solution was washed with water and dried. The residue (1.0 g) obtained after removal of the ether, solidified slowly. Upon the addition of a small amount of *n*-pentane, 0.220 g of a white solid, m.p. 81–85°, was obtained. Two recrystallizations from *n*-hexane produced an analytical sample, m.p. 90–91°. The infrared spectrum (in CCl_4) showed a band of medium intensity at 1 640 cm^{-1} and strong bands at 1 320 and 1 139 cm^{-1}.

Anal. Calcd. for 4-pentenyl α-(*p*-tolylsulfonyl)benzyl ether (XXIII), $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71; S, 9.70. Found: C, 68.86; H, 6.70; S, 10.01.

The pentane was removed, 2-ethoxynapthalene (0.100 g) was added as an internal standard, and the amount of XXI was determined by g.l.p.c.; yield 0.137 g (19.9%). When the experiment was repeated, the product was formed in a 20.6% yield.

The Preparation of Some Authentic Samples

Decanophenone

This compound was prepared in 77% yield by a Friedel–Crafts reaction between decanoyl chloride and benzene, according to the procedure of Breusch and Oguzer (11); m.p. 35–36°. Reported (11) m.p. 34.4–35.4°.

Decanophenone Dimethyl Ketal

Decanophenone (70.0 g, 0.30 mole), methyl orthoformate (32.0 g, 0.30 mole), and a small amount of anhydrous *p*-toluenesulfonic acid (0.40 g) were dissolved in a mixture of 200 ml of methanol and 25 ml of diethyl ether. This mixture was left at room temperature for 3 days, after which the acid was neutralized by adding sodium methoxide. The solvent was distilled off, the residue dissolved in ether, washed with water, and dried with magnesium sulfate. The ether was removed and the residue distilled *in vacuo* to give 71.4 g (84%) of the colorless liquid; b.p. 115–118° (0.3 mm); n_D^{25} 1.4804.

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.85; H, 10.95.

β-n-Octyl-α-methoxystyrene

Decanophenone dimethyl ketal (27.0 g, 0.097 mole) was stirred and heated with ammonium dihydrogen phosphate (2.0 g) at 200–210° for 45 min, under slightly reduced pressure. Initially, the pressure could be reduced only slightly because of foaming. After approximately 0.5 g the foaming ceased, probably indicating the complete removal of methanol. The liquid was distilled *in vacuo* to give 21.4 g (90%) of a 2:3 mixture of the isomeric products, b.p. 107–110° (0.2 mm); n_D^{25} 1.5035. The infrared spectrum of the neat liquid shows the olefinic double bond as a band of medium intensity at 1 641 cm^{-1}. The compound was found to have a molecular weight of 241 (osmometric); calcd. for $C_{17}H_{26}O$: molecular weight 246.4.

1-Methoxy-2-n-octyl-1-phenylcyclopropane

A crystal of iodine was added to a stirred suspension of a Zn–Cu couple (3) (7.2 g, 0.11 gram-atom) in 60 ml of anhydrous ether. As soon as the brown color had disappeared, methylene iodide (29.5 g, 0.110 mole) and an isomeric mixture of β-*n*-octyl-α-methoxystyrene (18.0 g, 0.073 mole) was added. The reaction mixture was refluxed for 13 h, after which the solid was filtered off. The ether solution was washed twice with a saturated aqueous ammonium chloride solution, twice with a saturated aqueous sodium bicarbonate solution, and finally twice with water. The residue obtained after drying and removal of the ether was distilled *in vacuo* to give 14.0 g (74%) of colorless product, b.p. 114–118° (0.3 mm); n_D^{25} 1.4926. The infrared spectrum shows a cyclopropyl ring deformation band at 1 020 cm^{-1}. The n.m.r. spectrum indicated that a small amount of β-*n*-octyl-α-methoxystyrene was still present which could not be removed by either distillation or elution chromatography on alumina. The n.m.r. spectrum showed that 1-methoxy-*cis*-2-*n*-octyl-1-phenylcyclopropane and 1-methoxy-*trans*-2-*n*-octyl-1-phenylcyclopropane were present in a ratio of 3:5.

n-Octylcyclopropane

To a suspension of a Zn–Cu couple (3) (10.6 g, 0.163 gram-atom) in 75 ml of anhydrous ether was added methylene iodide (43.7 g, 0.163 mole) and 1-decene (15.0 g, 0.107 mole), and the mixture was refluxed for 20 h. After filtration and washing with a saturated ammonium chloride solution, a saturated sodium bicarbonate solution, and water, the ether solution was dried over magnesium sulfate. Removal of the ether gave a residue that still contained a large amount of 1-decene. Enough bromine was added to convert all the 1-decene into the dibromo compound. The mixture was again dissolved in ether, washed twice with an aqueous sodium thiosulfate solution, and dried. The ether was removed and the residue distilled *in vacuo* to give 4.1 g (25%) of the product, b.p. 65–66° (5.0 mm); n_D^{25} 1.4280. A large amount of a higher boiling product, that partially decomposed, was left behind in the flask. The infrared spectrum of a neat sample of *n*-octylcyclopropane shows sharp absorption bands at 3 070 and 1 009 cm^{-1} respectively due to cyclopropyl hydrogen stretching and cyclopropyl ring deformation. The n.m.r. spectrum is described in the text.

Anal. Calcd. for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.68; H, 14.33.

1-Phenyl-2-oxabicyclo[4.1.0]heptane (XXI)

A crystal of iodine was added to a suspension of a Zn–Cu couple (13.0 g, 0.20 mole) in 80 ml anhydrous diethyl ether. As soon as the brown color had disappeared, methylene iodide (53.6 g, 0.20 mole) and 2-phenyl-Δ^2-dihydropyran (12) (25.0 g, 0.156 mole) were added and the mixture was stirred and refluxed for 20 h. A finely divided black suspension was filtered off and the ether solution successively washed with saturated aqueous ammonium chloride, saturated aqueous sodium bicarbonate, and water. After drying and removal of the ether, a yellow-colored liquid residue was obtained, that was distilled *in vacuo* to give 19.5 g (72%) of the colorless product, b.p. 75–76° (0.25 mm); n_D^{25} 1.5487. No starting material was recovered from the reaction. The infrared and n.m.r. spectra are compatible with that required by the structure XXI.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.44; H, 8.04.

Diethyl 3-Methoxy-3-phenyl-1,2-cyclopropanedicarboxylate

A solution of ethyl diazoacetate (5.5 g, 0.048 mole; prepared in 63% yield by the method of Searle (13); n_D^{25} 1.4616; reported (12) n_D^{25} 1.4616) in 10 ml of *n*-hexane was added dropwise, in approximately 30 min, to a refluxing solution of ethyl-*trans*-β-methoxycinnamate (6) (8.0 g, 0.039 mole) in 10 ml of *n*-hexane to which a small amount of cuprous chloride (0.25 g) had been added. A vigorous nitrogen evolution took place during the addition. Some ether was added and the solution was filtered. Upon removal of the ether a darkly colored liquid residue was obtained. A n.m.r. spectrum suggested that it contained mainly diethyl fumarate and ethyl *trans*-β-methoxycinnamate. Most of these products were removed by a vacuum distillation which yielded 1.3 g of a fraction boiling at 65–80° (1.7 mm) and 4.2 g of a fraction with b.p. 95–103° (0.3 mm). The residue (4.6 g) was chromatographed on alumina. A mixture of ethyl *trans*-β-methoxycinnamate and diethyl 3-methoxy-3-phenyl-*trans*-1,2-cyclopropanedicarboxylate was eluted with a *n*-hexane – benzene (1:1) mixture. Relatively pure diethyl 3-methoxy-3-phenyl-*trans*-1,2-cyclopropanedicarboxylate was eluted with benzene. The oil was dissolved in a small amount of *n*-hexane and cooled in a dry ice – acetone mixture. The solid thus obtained was twice recrystallized from a small amount of *n*-hexane to give an analytical sample of fine white needles, m.p. 40–41°. The total amount produced in the reaction was estimated at 1.1 g (10%).

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.49; H, 6.73.

Diethyl 3-methoxy-*trans*-3-phenyl-*cis*-1,2-cyclopropanedicarboxylate (0.33 g, 3%) was eluted with a *n*-hexane – diethyl ether (1:1) mixture. A relatively pure sample was obtained when this chromatography fraction was again chromatographed on alumina. The oily material, n_D^{25} 1.505, did not solidify at room temperature. Its infrared and n.m.r. spectra indicated that it was structurally similar to the isomeric material, and that it contained no olefinic hydrogens.

Anal. Calcd. for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.56; H, 6.89.

ACKNOWLEDGMENTS

The research described herein was supported by a National Research Council of Canada grant to R. J. Crawford. The n.m.r. and infrared spectra were measured by R. N. Swindlehurst and Mrs. Gail B. Conway of this Department.

REFERENCES

1. H. Zollinger. Azo and diazo chemistry. Interscience Publishers, Inc., New York, N.Y. 1961. Chap. 6. P. Yates. Abstracts of the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio. 1963. p. 93.
2. R. J. Crawford and R. Raap. Can. J. Chem. 43, 126 (1965).

3. L. J. BELLAMY. The infrared spectra of complex molecules. John Wiley and Sons, Inc., New York. 1959. p. 29. M. HANACK, H. EGGENSPERGER, and S. KANG. Chem. Ber. **96**, 2532 (1963).
4. R. D. SMITH and H. E. SIMMONS. Org. Syn. **41**, 72 (1961).
5. U. SCHOLLKOPF and E. WISKOTT. Angew. Chem. Intern. Ed. **2**, 485 (1963). U. SCHOLLKOPF and G. J. LEHMANN. Tetrahedron Letters, No. 4, 165 (1962). S. M. MCELVAIN and P. L. WEYNA. J. Am. Chem. Soc. **81**, 2579 (1959).
6. R. HUISGEN. Angew. Chem. Intern. Ed. **2**, 575, 633 (1963). W. M. JONES, T. H. GLENN, and D. G. BAARDA. J. Org. Chem. **28**, 2887 (1963).
7. F. ARNDT and L. LOEWE. Ber. **71**, 1631 (1938).
8. P. YATES. Abstracts of the 18th National Organic Symposium of the American Chemical Society, Columbus, Ohio. 1963. p. 360.
9. W. H. WANZLICK. Angew. Chem. Intern. Ed. **1**, 75 (1962). H. W. WANZLICK and H. J. KLEINER. Angew. Chem. Intern. Ed. **3**, 65 (1964).
10. W. KIRMSE. Ann. **666**, 9 (1963).
11. F. L. BREUSCH and M. OGUZER. Chem. Ber. **87**, 1225 (1954).
12. H. NORMANT. Compt. Rend. **231**, 909 (1950); Chem. Abstr. **46**, 3492 (1952).
13. N. E. SEARLE. Org. Syn. **36**, 25 (1956).