

sample²⁸ showed no melting point depression and coinjection in Hy-Fy glpc gave a single peak. The literature values¹⁸ for 5 β -methylcholestan-3-one are mp 88–89°, ν_{\max} 1708 cm⁻¹ (CHCl₃), $[\alpha]^{25D} +35^\circ$, ORD negative Cotton effect, trough ~ 300 m μ ($\alpha +32^\circ$).

Anal. Calcd for C₂₈H₄₈O (400.66): C, 83.93; H, 12.08. Found: C, 83.64; H, 11.91; mol wt, 400 (mass spectrum).

Reduction of 4 α ,5-Methanocholestan-3-one (17).—A solution of 0.2 g (0.5 mmole) of 17²⁷ in 10 ml of anhydrous ammonia was reduced with 70 mg (0.01 g-atom) of lithium for 20 min. Tlc anal-

ysis of the crude product showed only a trace of starting material. The material was chromatographed on alumina (activity III) and 140 mg of 5 α -methylcholestan-3-one was eluted with hexane-benzene (9:1). The product was crystallized from acetone: mp 162–163°; mixture melting point with authentic sample²⁸ showed no depression; ν_{\max} 1704 cm⁻¹; nmr, τ 8.74 (singlet, C₁₉), 8.98 (singlet, C₅- α -CH₂), 9.03 (doublet, $J = 5.5$ cps, C₂₁, C₂₆, C₂₇), 9.23 (singlet, C₁₈); $[\alpha]^{25D} +47.5^\circ$ (c 0.98); ORD positive Cotton effect, peak at 315 m μ ($\alpha +825$) and trough at 270 m μ ($\alpha -628^\circ$). The literature values for 5 α -methylcholestan-3-one are mp 168–169°, $\nu_{\max}^{\text{Nujol}}$ 1724 cm⁻¹, $[\alpha]^{25D} +49^\circ$, ORD positive Cotton effect, peak at ~ 300 m μ ($\alpha +970^\circ$) and trough at ~ 252 m μ ($\alpha -615^\circ$).

(28) We are indebted to Dr. W. Nagata for the authentic sample.

The Chemistry of Sulfonyl Isocyanates. III.¹ Reactions with Triarylcannabinols²

JOHN W. MCFARLAND, DAVID E. LENZ, AND DANIEL J. GROSSE³

DePauw University, Greencastle, Indiana

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Phenylsulfonyl isocyanate (I) and *p*-toluenesulfonyl isocyanate (II) reacted with triphenylmethanol and with triphenylmethanols containing phenyl, methyl, methoxyl, and chloro ring substituents to afford *N*-(triarylmethyl)sulfonamides (III) and carbon dioxide. *p,p',p''*-Trinitrotriphenylmethanol (V) and II gave *p,p',p''*-trinitrotriphenylmethyl *p*-tolylsulfonyleurethan (VI). Phenyl isocyanate (2 moles) combined with 1 mole of triphenylmethanol to give *N,N'*-diphenyl-*N*-(triphenylmethyl)urea (VIII). *p*-Tolyl isocyanate and triphenylmethanol gave *p*-tolyl(triphenylmethyl)amine (IX). Possible mechanisms for the reactions are discussed.

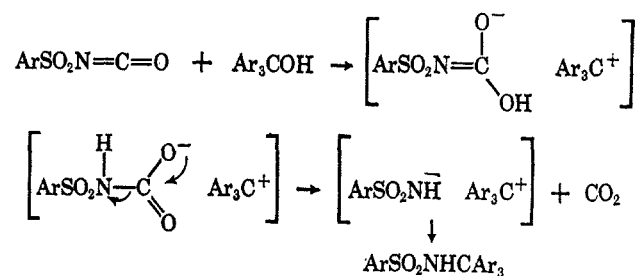
It has been shown that sulfonyl isocyanates react with hindered phenols and alcohols to give the normal urethan products.⁴ Extending the reaction from alkyl tertiary carbinols to tertiary carbinols containing aryl groups adjacent to the carbinol function afforded in most cases products which were not the urethans.

Phenylsulfonyl isocyanate (I) and *p*-toluenesulfonyl isocyanate (II) reacted with triphenylmethanol and triarylcannabinols containing electron-donating groups at temperatures from 0 to 100° in toluene. The products were the *N*-(triarylmethyl)sulfonamides (III) and carbon dioxide. (Table I). One of the products, *N*-(triphenylmethyl)benzenesulfonamide (IIIa), was independently synthesized from sodium benzenesulfonamide and triphenylchloromethane. The inability to obtain urethan even at 0° is interesting in view of the fact that diphenylmethanol and I gave urethan in good yields.⁴ The only other products obtained besides the sulfonamides were very small amounts of disulfonylureas.

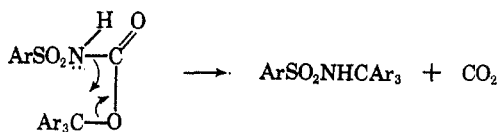
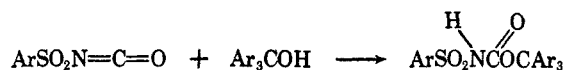
The most obvious mechanism for the formation of the products would be the intermediate production of urethan which would lose carbon dioxide gas. The fact that no urethan could be isolated, however, even at low temperatures indicates the mechanism to be a

doubtful one or that the urethan formed is extremely unstable. The solutions became colored during the reaction. Furthermore, solutions containing sulfonyl isocyanate and a triarylcannabinol absorbed in the 400–450-m μ range. Solutions containing triphenylmethanol showed absorption at 420 m μ which built up slowly during the early stages of reaction and then fell off in intensity during the latter stages.

Since triphenylmethylcarbonium ion, prepared from triphenylmethanol and sulfuric acid, absorbs at about 420 m μ ⁵ it is believed that (C₆H₅)C⁺ or an ion pair is being formed in solution. Whether this arises *via* urethan or by the alternate mechanism below cannot presently be stated.



It may be noted that all of the triarylcannabinols in Table I would be expected to give rather stable carbonium ions. Triarylcannabinols with strongly electron-withdrawing groups should give less stable carbonium ions and may follow a different mechanism in reacting with isocyanates. *p,p',p''*-Trinitrotriphenylmethane (IV) was prepared by nitrating triphenylmethane. Compound IV was converted to *p,p',p''*-trinitrotriphenylmethanol (V) by chromic acid. Upon the reaction of V and II, no carbon dioxide was evolved and 64.6% of *p,p',p''*-trinitrotriphenylmethyl *p*-tolylsulfonyleurethan was obtained. No absorption in the 400–450-m μ range was shown by the reaction solution. Such



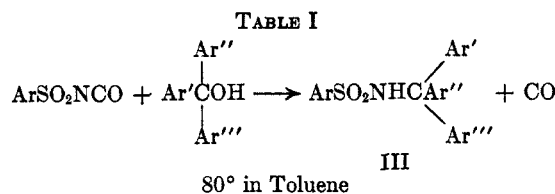
(1) For paper II, see J. W. McFarland and W. A. Burkhardt, III, *J. Org. Chem.*, **31**, 1903 (1966).

(2) Taken in part from the M.S. Theses of D. E. Lenz (1963) and D. J. Grosse (1965), DePauw University, and presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts of Papers, p 2-S.

(3) National Defense Education Act Fellow, 1963–1964.

(4) J. W. McFarland and J. B. Howard, *J. Org. Chem.*, **30**, 957 (1965).

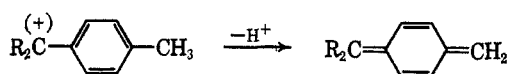
(5) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).



Ar	Ar'	Ar''	Ar'''	N-(Triarylmethyl)sulfonamide product % yield	Mp. °C
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	87.0	242-243
C ₆ H ₅	<i>p</i> -C ₆ H ₄ C ₆ H ₄	<i>p</i> -C ₆ H ₄ C ₆ H ₄	<i>p</i> -C ₆ H ₄ C ₆ H ₄	95.7	232.5-233.5
C ₆ H ₅	<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	C ₆ H ₅	84.6	184-185
C ₆ H ₅	<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -CH ₃ OC ₆ H ₄	<i>p</i> -CH ₃ OC ₆ H ₄	80.0	178-180
C ₆ H ₅	<i>o</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	54.5	237-238
C ₆ H ₅	<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄	Mixture of products	
<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	85.0	241-242
<i>p</i> -CH ₃ C ₆ H ₄	<i>p</i> -C ₆ H ₄ C ₆ H ₄	<i>p</i> -C ₆ H ₄ C ₆ H ₄	<i>p</i> -C ₆ H ₄ C ₆ H ₄	86.1	264-265

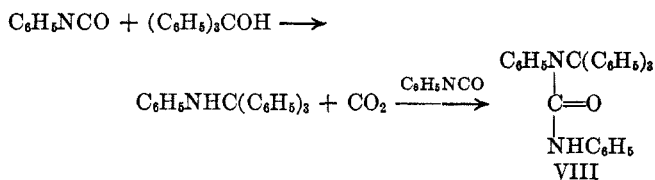
a result neither proves nor disproves the possibility of all the reactions proceeding through a urethan intermediate. The others may proceed through urethans which are extremely unstable and decompose rapidly to triarylmethylcarbonium ions.

A word should be given regarding alkyl-substituted triarylcannabinols. As indicated in Table I, one *o*-methyl group lowered the yield considerably. Tri-*p*-tolylmethanol (VII) synthesized by the Grignard method, and I gave a mixture of products, from which as much as 80% of benzenesulfonamide was recovered. The other products were mixtures of carbinol and probably some alkenes. A more thorough investigation of these reactions is being carried out and will be reported later. Presently it is believed that a triarylcannabinol ion is formed which eliminates proton to give a stable quinoidal system.



To determine whether the above type of reaction required both a triarylcannabinol and a sulfonyl isocyanate, ordinary isocyanates such as phenyl and *p*-tolyl were allowed to react with triphenylmethanol. Knoevenagel and Schurenberger⁶ reported no reaction between phenyl isocyanate and triphenylmethanol. Using approximately a 4:1 ratio of isocyanate:carbinol the reaction proceeded extremely slowly at 100°. After 4 days a 26.0% yield of *N,N'*-diphenyl-*N*-(triphenylmethyl)urea (VIII) was obtained.

Apparently a reaction similar to that of sulfonyl isocyanates had occurred, followed by the reaction of another molecule of isocyanate with the amine intermediate.



p-Tolyl isocyanate and triphenylmethanol (2:1 ratio) reacted to give 66.2% yield of *p*-tolyl(triphenylmethyl)amine (IX). The phenyl and *p*-tolyl isocyanates were not extensively studied but it appears that the essential requirement for the reaction is the presence of a tri-

arylcannabinol. The driving force for the reaction appears to be the stability of the triarylcannabinol ion. If the carbonium ion can lose a proton as is the case with the methylated triarylcannabinols, complications arise. Furthermore, strongly electron-withdrawing nitro groups reduce carbonium ion stability and urethan is isolated. It is interesting that the reaction between a sulfonyl isocyanate and a triarylcannabinol produces no products having more than one isocyanate fragment per alcohol fragment, although isocyanate:alcohol ratios were varied from 1:10 to 10:1. The products, ArSO₂NHC-Ar₃, might be expected to react further since *N*-substituted amides⁷⁻⁹ and sulfonamides¹⁰ have been shown to react with sulfonyl isocyanates. Anchored by a sulfonyl group and a triarylmethyl group, however, the nitrogen is hindered by both steric and electronic effects from attacking even a powerful electrophile such as the sulfonyl isocyanate.

Experimental Section

Phenylsulfonyl isocyanate (I) was prepared by the method of Billeter¹⁰ and purified by distillation through a 30-in. spinning-band column. *p*-Toluenesulfonyl isocyanate (II) was obtained from the Upjohn Co., Carwin Organic Chemicals, and used without further purification. Triphenylmethanol was a commercial product. The substituted triphenylmethanols except the nitro compound were prepared by the Grignard method. Toluene, benzene, ether, and petroleum ether (bp 37.5-50°) were dried over sodium before use.

Reactions with Triarylcannabinols.—The reaction of I with *p*-, *p'*-, and *p''*-tribiphenylmethanol is typical of the reactions shown in Table I. Into a dry and N₂-flushed 50-ml erlenmeyer flask were placed 1.46 g (0.003 mole) of *p,p',p''*-tribiphenylmethanol and 20 ml of toluene. The flask was fitted with a cork wrapped with aluminum foil and placed in an 80° oil bath. To the flask was added a solution of 0.55 g (0.003 mole) of I in 5 ml of toluene. The solution turned purple and gas evolution was noted. The gas was shown to be CO₂ by bubbling it into lime water. Occasionally the cork was loosened to vent the gas. The solution was heated at 80° for 5 hr, cooled to room temperature (RT), and diluted with 1 vol of petroleum ether. The precipitated slightly pink solid was collected by suction filtration and amounted to 1.80 g (95.7%), mp 215-228°. Recrystallization from benzene gave white platelets of *N*-(*p,p',p''*-tribiphenylmethyl)benzenesulfonamide (IIIb) with constant mp 232.5-233.5°.

Anal. Calcd for C₄₃H₃₃NO₂S: C, 82.30; H, 5.26; N, 2.23; S, 5.10. Found: C, 82.17; H, 5.38; N, 2.24; S, 5.15.

The infrared spectrum showed NH absorption at 3350 cm⁻¹. (The range for the *N*-(triarylmethyl)sulfonamides (III) was

(7) W. Logemann and D. Artini, *Ber.*, **90**, 2527 (1957).

(8) W. Logemann, D. Artini, and G. Tosolini, *ibid.*, **91**, 951 (1958).

(9) C. King, *J. Org. Chem.*, **25**, 352 (1960).

(10) O. C. Billeter, *Ber.*, **37**, 690 (1904).

(6) E. Knoevenagel and A. Schurenberger, *Ann.*, **297**, 148 (1897).

3250–3350 cm^{-1}) and the absence of carbonyl absorption. The nmr spectrum had an NH band at $\tau = 3.50$ ppm.

In another experiment, I and triphenylmethanol were allowed to react in equal molar amounts as above in toluene at 0° for 7 days. The precipitated product was collected and amounted to a 10.1% yield of IIIa. Analysis of the filtrate showed only unreacted I and triphenylmethanol.

All of the products in Table I were similarly identified by elemental analysis, infrared spectra, and nmr.

Independent Synthesis of N-(Triphenylmethyl)benzenesulfonamide (IIIa).—Compound IIIa was synthesized by the method of Dohlbon and Ekstrand.¹¹ Sodium benzenesulfonamide (10.7 g, 0.06 mole), prepared from sodium ethoxide and benzene sulfonamide,¹² and 16.7 g (0.06 mole) of triphenylchloromethane were added to 140 ml of benzene and the mixture was heated under reflux for 3 hr. Insolubles were removed by filtering the hot solution. Upon cooling the filtrate white needles were precipitated and were collected, weight 13.0 g (54.4%), mp 225–235°. Recrystallization from toluene afforded IIIa with constant mp 240–242°, lit.¹¹ mp 242–243°, mixture melting point with product from I and triphenylmethanol 240–242°. The infrared spectra of the two products were identical, showing NH absorption at 3250 cm^{-1} and no carbonyl absorption.

***p,p',p''*-Trinitrotriphenylmethane (IV).**—To a 1-l. three-necked flask fitted with stirrer, dropping funnel, and thermometer, was added 200 ml of 70% nitric acid. The contents of the flask were cooled to -15° by means of an ice-salt bath and 40.0 g (0.164 mole) of triphenylmethane was added in portions with good stirring. Concentrated sulfuric acid (200 ml) was added dropwise with stirring over a period of 2.5 hr, maintaining the reaction temperature at -5 to 0° . After the acid addition the mixture was allowed to warm to RT and then stirred at 35° for 0.5 hr. The mixture was added to 3 l. of ice and water, and the slightly yellow solid was filtered by suction, and washed with water, weight 50 g, mp 160–175°.

To remove mono- and dinitrated products which are soluble in acetic acid, the product was heated with boiling acetic acid for 30 min and filtered hot. The insoluble IV was washed on the filter with cold water, dried, and amounted to 32.8 g (52.8%), mp 193–200°. Recrystallization from toluene gave IV with constant mp 211–213°, lit.¹³ mp 212°.

***p,p',p''*-Trinitrotriphenylmethanol (V).**—Compound V was prepared by modification of the methods of Fischer and Fischer,¹⁴ and of Montagne.¹³ Into a 3-l. three-necked flask fitted with a stirrer, dropping funnel, and thermometer was placed a slurry of 26.3 g (0.07 mole) of IV and 1200 ml of glacial acetic acid. The mixture was heated to 50° and a warm solution of 26 g of chromium trioxide in 280 ml of glacial acetic acid and 1 ml of concentrated sulfuric acid was added during 45 min with stirring and maintaining reaction temperature at 50° . The mixture was heated at 50° for an additional 2 hr and added to 4 gal of ice and water. The slightly yellow solid was collected by suction filtration, and while still damp, dissolved in 250 ml of glacial acetic acid and filtered hot. The filtered solution was added to 400 ml of water and the precipitate was collected by suction filtration and dried in air, weight 21.0 g (76.0%), mp 175–183°. Recrystallization from glacial acetic acid gave V with constant mp 189–190°, lit.¹⁵ mp 191°.

Reaction of II and V.—To a 50-ml erlenmeyer flask fitted with an aluminum foil covered cork were added 40 ml of dry toluene,

0.60 g (0.00305 mole) of II, and 1.19 g (0.00305 mole) of V. Compound V did not dissolve until the mixture was heated in a 100° oil bath. After overnight at 100° solid had precipitated in the flask. Heating at 100° for another 5 days did not appear to change the amount of precipitate. The mixture was cooled to RT, the precipitate was collected by suction filtration, and amounted to 1.15 g (64.6%), mp 198–199° dec. Recrystallization from acetone-petroleum ether gave *p,p',p''*-trinitrotriphenylmethyl-*p*-tolylsulfonamide (VI) with constant mp 198–199° dec.

Anal. Calcd for $\text{C}_{27}\text{H}_{20}\text{N}_4\text{O}_6\text{S}$: C, 54.73; H, 3.38; N, 9.46; S, 5.41. Found: C, 54.94; H, 3.70; N, 9.77; S, 5.74.

Compound VI showed NH absorption at 3265 cm^{-1} and carbonyl absorption at 1760 cm^{-1} .

Dilution of the filtrate obtained from the collection of VI with 2 volumes of petroleum ether gave 0.50 g of solid, mp 130–150°. Infrared spectroscopy indicated that the solid was a mixture of alcohol VI (OH band at 3625 cm^{-1}) and *p*-toluenesulfonamide ($\text{N}-\overset{\text{H}}{\text{H}}$ at 3450 and 3350 cm^{-1}), with only a trace of carbonyl present.

Tri-*p*-tolylmethanol (VII).—To a 1-l. three-necked flask fitted with a mechanical stirrer, a dropping funnel, and a condenser, was added 5.35 g (0.22 g-atom) of magnesium metal. The entire apparatus was flamed under nitrogen. To the cooled flask was added 15 ml of dry ether, and from the dropping funnel was added with stirring and under N_2 during 30 min a solution of 37.6 g (0.22 mole) of *p*-bromotoluene in 50 ml of ether. The mixture was heated under reflux for 10 min and cooled to RT. A solution of 42.1 g (0.20 mole) of di-*p*-tolyl ketone in 225 ml of ether was added during 45 min at RT, and the mixture was then heated under reflux for 30 min.

The mixture was hydrolyzed with 150 ml of cold 2 *N* HCl solution. The two layers were separated and the ether layer was washed with three 50-ml portions of water and dried over MgSO_4 . Removal of the ether gave a semisolid which was dissolved in 50 ml of hot petroleum ether (60 – 70°). Upon cooling white crystals precipitated and amounted to 31.6 g (52.3%). Recrystallization from petroleum ether gave needles with constant mp 94–95°, lit.¹⁵ mp 97°.

Phenyl Isocyanate and Triphenylmethanol.—Phenyl isocyanate (1.84 g, 0.015 mole) and 1.0 g (0.0039 mole) of triphenylmethanol were dissolved in 5 ml of dry toluene in a test tube. The tube was stoppered with a cork and heated at 100° for 4 days. The red solution was cooled to RT and diluted with 5 ml of petroleum ether. The precipitate was collected, weight 0.46 g (26.0%), mp 186–187°. Recrystallization from ethanol gave *N,N'*-diphenyl-*N*-(triphenylmethyl)urea (VIII) with constant mp 186–187°. The infrared spectrum showed weak absorption at 3500 cm^{-1} and strong carbonyl absorption at 1690 cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}$: C, 84.58; H, 5.73; N, 6.17. Found: C, 84.52; H, 5.93; N, 6.16.

***p*-Tolyl Isocyanate and Triphenylmethanol.**—Into a dry test tube were placed 1.02 g (0.0077 mole) of *p*-tolyl isocyanate, 1.0 g (0.0039 mole) of triphenylmethanol, and 7 ml of dry toluene. The cork-stoppered tube was heated at 100° for 2 days, cooled to RT, and the precipitate was collected by suction filtration, weight 0.90 g (66.2%), mp 168–170°. Recrystallization from ethanol gave *p*-tolyl(triphenylmethyl)amine (IX) with constant mp 179–180°, lit.¹⁶ mp 180–181°. The infrared spectrum exhibited weak NH absorption at 3500 cm^{-1} but no carbonyl absorption.

Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{N}$: C, 89.39; H, 6.59; N, 4.01. Found: C, 89.10; H, 6.73; N, 4.00.

(16) P. E. Verkade, H. Nijon, F. D. Tollenaar, J. H. van Rij, and M. Leeuwen, *Rec. Trav. Chim.*, **71**, 1007 (1952).

(11) R. Dohlbon and T. Ekstrand, *Svensk Kem. Tidskr.*, **56**, 304 (1944); *Chem. Abstr.*, **40**, 3415 (1946).

(12) L. Field and F. A. Grunwald, *J. Am. Chem. Soc.*, **75**, 934 (1953).

(13) M. Montagne, *Rec. Trav. Chim.*, **24**, 125 (1905).

(14) E. Fischer and O. Fischer, *Ann.*, **194**, 256 (1878).

(15) G. L. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 4397 (1956).